BLUFF (OU3)

The Former Plant Site Area (OU3)

EAST SUBAREA

White City Park SP-4

SS-04

E1 E2 E3 E4 E5 E6 E7

Haines St

Della St

Marquette St

Legend

- Observation of Contiguous Area of Potential Site Related Material
- Isolated Pieces of Site Related Material
- Potential Site-Related Material Along Railroad Tracks
- Existing Railroad
- Non-Existing Railroad
- Areas of Potential Plant Material
- Removal Action Limit Sample Location
- OU2: The Phosphogypsum Stack
- OU3: The Former Plant Site Area/Bluff Area
- OU4: Offsite Soils
- DePue Parcel
- Parks
- Commercial Property
- Vacant DePue Parcels

Estimated Number of Pilot Study Properties: 12

Aerial: GIS and Parcel Data Source- Bureau County Recorders Office

0 100 200 300 400 Feet

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ENVIRON

Drafted By: ENE/CCS | DATE: 5/16/2013

Potential Off-Site Soil Sampling Locations
East Subarea
OU4 Pilot Study
DePue Site - DePue, Illinois

Figure 2-5

PROJECT: 21-12046C

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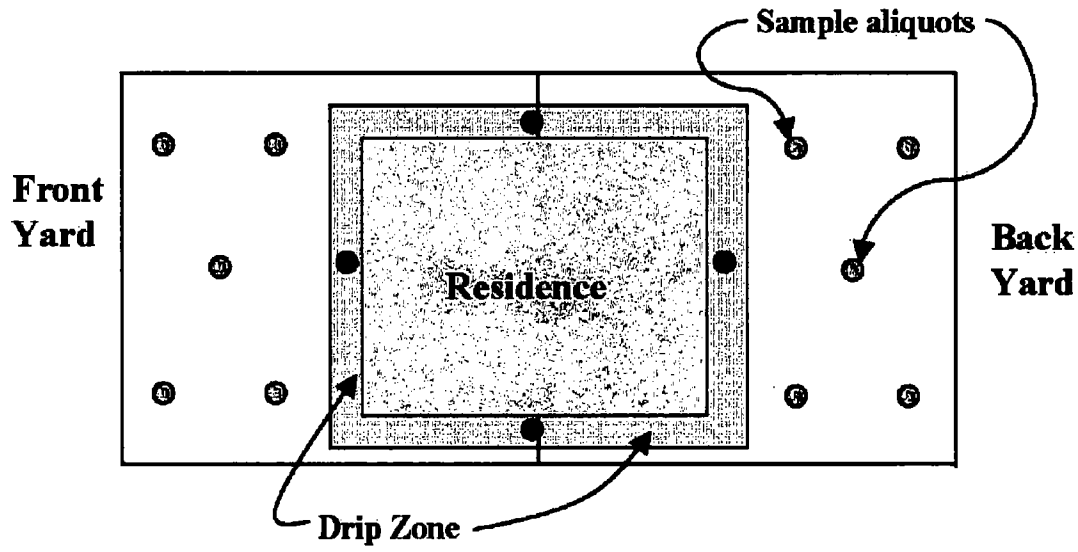
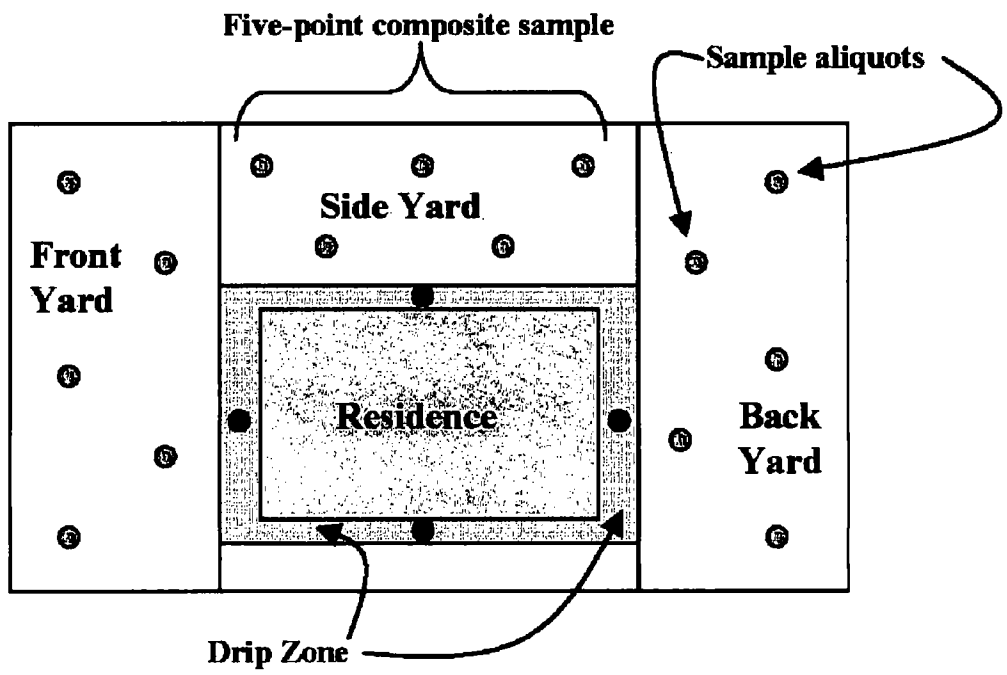
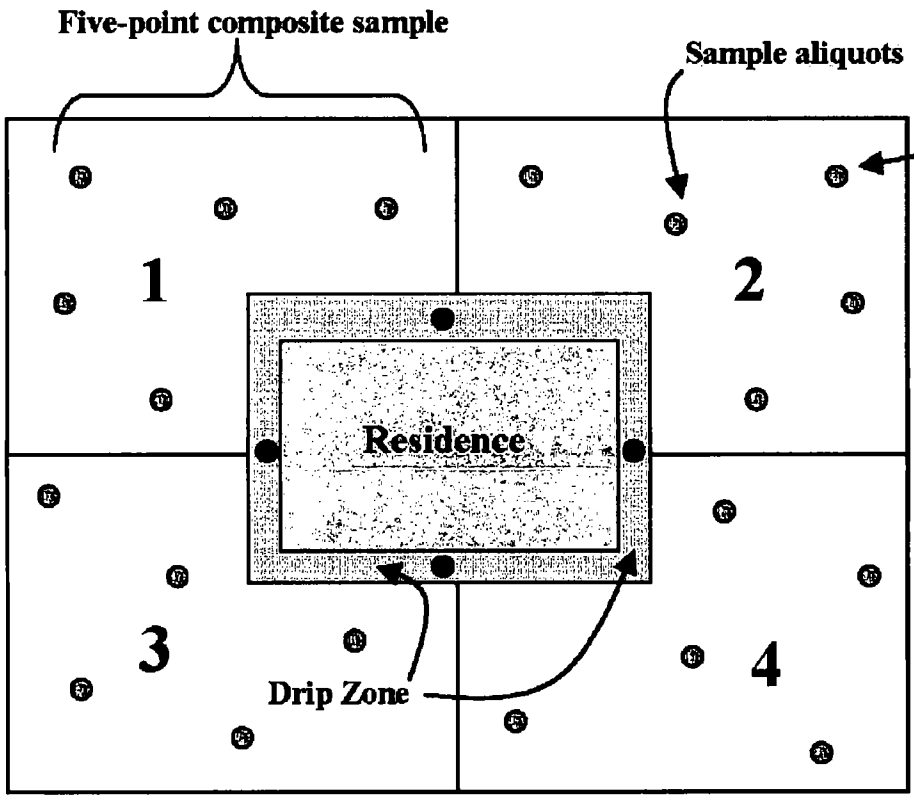


SCENARIO 1: RECOMMENDED MINIMUM SOIL SAMPLING IN YARDS LESS THAN OR EQUAL TO 5,000 SQUARE FEET WITH SIDE YARD LESS THAN ONE-THIRD THE TOTAL YARD AREA (OR NO SIDE YARD).



SCENARIO 2: RECOMMENDED MINIMUM SOIL SAMPLING IN YARDS LESS THAN OR EQUAL TO 5,000 SQUARE FEET WITH SIDE YARD AT LEAST ONE-THIRD THE TOTAL YARD AREA.



SCENARIO 3: RECOMMENDED MINIMUM SOIL SAMPLING IN YARDS GREATER THAN 5,000 SQUARE FEET.

SOURCE: USEPA Lead Sites Workgroup, Sec. 4.2.2 Residential Yards, *Superfund Lead-Contaminated Residential Sites Handbook*, OSWER 9285.7-50, August 2003.

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DRAFTED BY: ELS/CCS | DATE: 8/15/13

RESIDENTIAL YARD SOIL SAMPLING SCENARIOS
OU4 PILOT STUDY
DEPUE SITE
DEPUE, ILLINOIS

FIGURE
2-6
21-12046C

BLUFF AREA

LITHOPONE RIDGES AREA

ROASTER/ACID/ FERTILIZER PLANT AREA

EASTERN AREA

SMELTER (HORIZONTAL AND VERTICAL RETORTS) AREA

WESTERN AREA

SLAG PILE AREA

CAMU AREA

RAILYARD

RAILROAD CORRIDOR

MARQUETTE STREET

DIVISION STREET

NORTH DITCH

SOUTH DITCH

VANADIUM PENTOXIDE CATALYST DISPOSAL AREA

FORMER MUNICIPAL DUMP

FORMER SETTLING PONDS

UPLAND PORTION OF THE SOUTHEAST AREA

CADMIUM PLANT/ ZINC DISTILLATION COLUMNS AREA

500 250 0 500

APPROXIMATE SCALE IN FEET

N

LEGEND:

APPROXIMATE AREA OF FORMER PLANT SITE AND UPLAND PORTION OF THE SOUTHEAST AREA

APPROXIMATE AREA OF BLUFF AREA

HISTORICAL FEATURE

PHASE I RI SAMPLING LOCATIONS:

WP1 ● TEMPORARY WELL POINT

J1 X BORING

LY2 ✦ LYSIMETER

W2D ▲ MONITORING WELL (BASE OF LOWER AQUIFER)

W5S ◆ MONITORING WELL (TOP OF LOWER AQUIFER)

W11S ■ MONITORING WELL (UWBZ OR AQUITARD)

W3S ▣ MONITORING WELL (BLUFF UNDIFFERENTIATED)

PZ4S ⊗ PIEZOMETER (UWBZ OR AQUITARD)

PZ4I △ PIEZOMETER (TOP OF LOWER AQUIFER)

OTHER LOCATIONS

PS-11 ◐ EXISTING MONITORING WELL OR PIEZOMETER (TOP OF LOWER AQUIFER)

HS11(S) ◒ EXISTING MONITORING WELL OR PIEZOMETER (UWBZ OR AQUITARD)

HH-03 ○ HH/DANIEL B. STEPHENS TEMPORARY AND PERMANENT MONITORING WELL

SS-05 ◪ EXXONMOBIL SUPPLEMENTAL ZINC PROCESSING WASTE SAMPLE

SL-G ⊡ EXXONMOBIL SUPPLEMENTAL INVESTIGATION SAMPLE

TA-1 ◒ EXXONMOBIL SUPPLEMENTAL SAMPLE

Z-11 ⊞ VIACOM SOIL BORING

Z-9 ⊕ VIACOM TEMPORARY MONITORING WELL

S-250 ▬ VIACOM SAMPLING LOCATION

ABC-1 ◬ VIACOM ABC BORING

SHELBY-1 ◐ SHELBY TUBE SAMPLE

N001 ○ SPRING SAMPLE LOCATION

CSB-1 ✸ CAMU INVESTIGATION BORING

PHASE II RI SAMPLING LOCATIONS

REPLACEMENT WELL

TEST PIT

PHASE II RI WELL

ABANDONED MONITORING WELL OR PIEZOMETER

PROPOSED HEXAVALENT CHROMIUM SAMPLE LOCATION

UWBZ = UPPER WATER-BEARING ZONE

CAMU = CORRECTIVE ACTION MANAGEMENT UNIT

NOTES:

1. BASE MAP PREPARED FROM ELECTRONIC FILE OF DRAWING NO. 95-13562, AT A SCALE OF 1"=50', DATED 6/19/03 BY "FRANK AND WEST ENVIRONMENTAL ENGINEERS, INC.".
2. ALL LOCATIONS ARE APPROXIMATE.

PROPOSED OU3 SAMPLE LOCATIONS FOR HEXAVALENT CHROMIUM EVALUATION

OU4 PILOT STUDY
DEPUE SITE
DEPUE, ILLINOIS

ENVIRON

FIGURE 2-7

DRAFTED BY: ELS/CCS | DATE: 8/15/13 | 21-12046C

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APPENDIX A

APPENDIX A

Appendix A

Access Agreement

ACCESS AGREEMENT

Property Address _____ PO Box _____

_____ _____

_____ ("Grantor"), gives CBS Operations ("CBS") and their employees, representatives, environmental consultants and contractors, and the Illinois Environmental Protection Agency ("IEPA") and the U.S. Environmental Protection Agency ("USEPA") and their representatives the right to enter property at _____ (the "Property") to perform environmental investigations and response actions (if necessary). CBS is cooperating with IEPA and USEPA to investigate the residential soils in the vicinity of the DePue Site, and this property has been identified as located within the investigation area.

By signing below, the Grantor agrees to the following:

1. Grantor has the authority to grant entry to the Property.

2. The work that is the subject of this Access Agreement (the "Work") is described in the IEPA-approved Off-Site Soils Design Study: OU4 Off-Site Soils or IEPA-approved Pilot Study dated October 2013. The Work will include the following:

- Collection of soil samples;
- Potential performance of necessary response actions (e.g., soil excavation, backfilling, and restoration).

3. Representatives and contractors of CBS may conduct the Work described above on the Property and any damage caused by the Work shall be restored or repaired to as close to its condition existing at the time the Work began as is reasonably possible.

4. Representatives of CBS may enter the Property whether or not representatives of Grantor are present. Grantor will receive 14 days' notice of the commencement of each phase of work requiring access to the property.

5. In exercising the rights granted in this Access Agreement, representatives of CBS shall not unreasonably interfere with the Grantor's access to or use of the Property. Grantor agrees to use its best efforts not to interfere with the Work.

6. Representatives and contractors of CBS will need to enter the Property on more than one occasion in order to conduct the Work.

7. The rights and privileges granted by this Access Agreement shall cease upon completion of the Work as determined by the governmental authorities.

8. CBS shall release and hold Grantor harmless for loss of or damage to property and equipment of CBS or their consultants while such property or equipment is in or on the Property, except where such loss of or damage to property and equipment results from Grantor's negligence or willful misconduct.

9. This Access Agreement is binding upon Grantor and CBS and their respective

successors, transferees and assigns.

10. This Access Agreement constitutes the parties' entire agreement on this subject. There are no written or oral representations or understandings that are not fully expressed in this Agreement. No change, waiver, or discharge is valid unless in writing and signed by the party against whom it is sought to be enforced.

11. This Access Agreement is not and shall not be construed as an admission by Grantor and/or CBS of any issue of fact or law or as an admission or adjudication of any liability and shall not be admissible in any other suit or proceeding except a suit or proceeding to enforce its terms.

_____
Date

GRANTOR

_____ I grant access to my property _____ I do not grant access to my property

_____
Signature

_____
Print Name

Address:_____

_____

Phone Number:_____

TENNANT (If Applicable)

Name:_____

Phone Number:_____

APPENDIX B

APPENDIX B

Appendix B

Property Evaluation Form

Property Inspection Checklist
OU4 Design Study
DePue Site, DePue, IL

Address: _____

_____ Date: _____
Owner Time: _____

_____ _____
Occupant (if different from occupant) Assessor

How long has owner owned the property? _____
How many people live in the home? _____ What are their ages? _____
What year was the home built? _____
Any wells on the property? _____ Yes _____ No
If yes, is it active and what purpose is it used for? _____
Number of Stories _____
Distance from ground to soffit _____ ft.
Roof overhead distance _____ ft.
How is the home heated? _____
Any fill material put on the property? _____ Yes _____ No
If yes, please specify type, source, and location _____
Any difficulty growing grass on the property? _____ Yes _____ No
Any fertilizer or lawn care products used? _____ Yes _____ No
If yes, please identify products _____
Animals on the property? _____ Yes _____ No
Garden on property? _____ Yes _____ No
Size and location of garden _____
Burn barrel/area on property? _____ Yes _____ No
If yes, description and location _____
Play area on property? _____ Yes _____ No
If yes, description and location _____

Item	YES	NO	NA	PROBLEM/CONDITION
YARD AREA				
1. Lawn Area				
A. Flower/plant boxes painted				
C. Grass cover				
D. Shrubbery				
E. Trees				
F. Air conditioner painted				
G. Air conditioner condenser foundation painted, cracked				
H. Painted lawn furniture				
I. Other:				
2. Utility				
A. Water meter				
B. Gas meter				
C. Sewer lines				
D. Other:				

Property Inspection Checklist
OU4 Design Study
DePue Site, DePue, IL

Address: _____

Item	YES	NO	NA	PROBLEM/CONDITION
3. Driveway				
A. Concrete painted, cracked, damaged				
B. Blacktop cracked, damaged				
C. Uneven settling				
D. Other:				
4. Sidewalk & Walkways				
A. Concrete painted, cracked, eroded				
B. Tree roots cracking, lifting slab				
C. Other:				
5. Garage				
A. Settlement cracks in walls				
B. Concrete floor painted				
C. Garage painted				
D. Other:				
6. Swimming Pool (Above Ground)				
A. Leakage				
B. Visible damage				
C. Ladder painted				
D. Other:				
7. Swimming Pool (Below Ground)				
A. Leakage				
B. Visible damage				
C. Concrete around pool painted				
D. Other:				
HOUSE EXTERIOR AREA				
8. Bricks & Siding				
A. Bricks painted, cracking				
B. Mortar loose, needs repointing				
C. Door frames painted				
D. Siding painted, damaged				
E. Finish wearing off siding				
F. Window frames painted, damaged				
G. Other:				
9. Roofing (as seen from ground surface)				
A. Brick chimney painted, broken, leaning				
B. Joint open between chimney & exterior wall				
C. Painted Roofing				
D. Boards around roof painted				

Property Inspection Checklist
OU4 Design Study
DePue Site, DePue, IL

Address: _____

Item	YES	NO	NA	PROBLEM/CONDITION
E. Other:				
10. Gutters & Molding				
A. Exterior molding board painted, damaged				
B. Gutters painted				
C. Downspout painted				
D. Other:				
11. Entrance Steps				
A. Concrete painted, cracked				
B. Brick cracked, mortar loose				
C. Risers painted				
D. Stair supports painted				
E. Handrail painted, loose				
F. Handrail supports painted				
G. Other:				
12. Exterior Doors				
A. Trim painted, rotted, missing				
B. Jambs painted, rotted, damaged				
C. Other:				
13. Windows				
A. Trim/sills painted, loose				
B. Broken glass				
C. Frame separation from walls				
D. Window air conditioner painted				
E. Other:				
14. Exterior Porch				
A. Handrail posts painted, loose, damaged				
B. Columns painted, loose, damaged				
C. Lattice painted, cracked, hanging				
D. Railing caps painted, damaged				
E. Handrails painted, loose, damaged				
F. Other:				
15. Foundation (Slab on Grade)				
A. Settlement cracks				
B. Painted concrete				
C. Other:				
16. Foundation (Elevated Slab w/Crawl Space				
A. Concrete cracked or spalling				
B. Evidence of moisture or visible moisture on crawl space entrance				

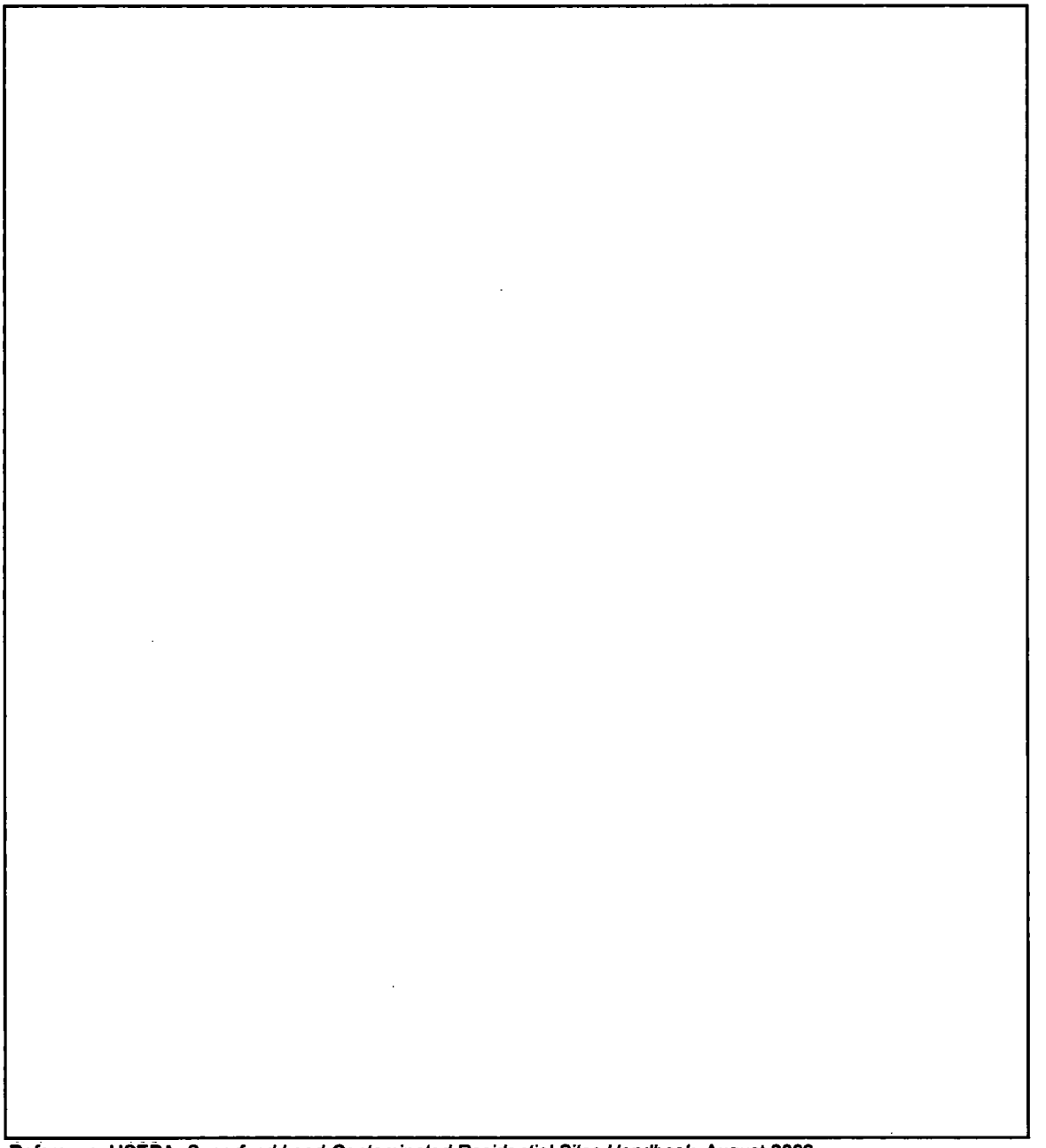
Property Inspection Checklist
OU4 Design Study
DePue Site, DePue, IL

Address: _____

Item	YES	NO	NA	PROBLEM/CONDITION
C. Evidence of water accumulation (i.e., water stains) at crawl space entrance				
D. Other:				
17. Foundation with basement				
A. Minor cracks				
B. Settlement cracks at corners, walls				
C. Walls bulging inward				
D. Seepage into basement				
E. Concrete/mortar deteriorating				
F. Other:				
16. Exterior Structures				
A. Fence painted, loose				
B. Laundry line posts painted				
C. Storage sheds painted				
D. Play houses/play equipment painted				
E. Mailboxes painted				
F. Pet house painted				
G. Debris piles, non-operable automobiles, wood piles, etc				
H. Other:				

Notes/Observations: _____

17. Sketch



Reference: USEPA. *Superfund Lead-Contaminated Residential Sites Handbook.* August 2003.

APPENDIX C

APPENDIX C

Appendix C

Field Sampling Plan

Field Sampling Plan
OU4: Off-Site Soils
DePue Site
DePue, Illinois

Prepared for:
Illinois Environmental Protection Agency

Prepared by:
ENVIRON International Corporation
Chicago, Illinois

Date:
October 2013

Project Number:
21-12046C

ENVIRON

Contents

1 Introduction

This Field Sampling Plan (the "FSP") has been prepared to cover the field tasks included in the Off-Site Soils Design Study for Operable Unit (OU) 4 (the "Design Study") and the Off-Site Soils Pilot Study (the "Pilot Study") prepared by ENVIRON International Corporation (ENVIRON). This FSP has been prepared in addition to the existing site-wide Field Sampling Plan Addendum (the "2006 FSP") (ENVIRON, 2006a), and the FSP Addendum for the Removal Action Limit Assessment (the "RAL FSP") prepared by Basland, Bouck & Lee, Inc. (BBL) dated May 2005.

Additional details concerning specific aspects of the work described in this FSP are provided in supporting documents such as the RAL Quality Assurance Project Plan (QAPP) Addendum (ENVIRON, 2013), and site-wide Health and Safety Plan (HASP) Addendum (ENVIRON, 2006b). Certain activities, which are not addressed in the previous versions of these documents, require an addendum. These addenda have been prepared concurrently with this FSP.

2 Field Methodology

2.1 General

This section presents the field methods used to conduct the OU4 field sampling activities of the Pilot Study and Design Study. Detailed sample collection procedures are presented in standard operating procedures (SOPs) that are included as appendices to this FSP.

Soil samples will be collected using a hand-driven split-spoon, macrocore sampler, or hand auger. Enough volume will be collected from each depth interval to fulfill sample mass requirements. The collection procedures are presented in Appendix A. The techniques described in Appendix A are generally similar to the soil sampling techniques specified in the site-wide QAPP (Technical Procedure [TP] Tp-1.2-18: Sampling Surface Soil for Chemical Analysis; TP-1.2-5: Drilling, Sampling, and Logging of Soils (Golder, 1999b)); however, the details provided in Appendix A are specific to the soil sampling component of the off-site soils investigations.

Prior to commencing field activities, access to the properties and areas to be sampled will be confirmed. Residential and private property access will be obtained via an individual access agreement with the property owner. Public property access will be obtained via an agreement with the Village of DePue, Bureau County, and/or other local governments, as appropriate. In addition, the DePue Group owns property that may be sampled during the off-site soil investigations.

In accordance with the Illinois Utility Facilities Damage Prevention Act, local utility companies will be contacted via the Illinois One-Call System, JULIE (800.892.0123), at least two working days before soil sampling to identify and mark the location of any existing underground utilities.

2.2 Off-Site Soil Sampling

The following section summarizes a description of the sample locations, sample collection procedures, and analytical methods that will be used during the Pilot Study and the Design Study. As outlined in the Design Study, the OU 4 soil sampling investigation will include sampling of soils in the area surrounding the Former Plant Site Area (FPSA), designated as OU3. Areas proposed for sampling include residential and residential-like properties, special use areas, and ecological habitat areas. The Pilot Study will include residential properties only.

Sample Locations

The Pilot Study includes sampling of 30 to 50 randomly selected properties distributed throughout the OU4 study area. The Design Study outlines a comprehensive soil sampling program designed such that all of the residential property owners within the OU4 study area are given the opportunity to have soil on their properties sampled and, if necessary, remediated. The number and location of samples collected will be dependent upon property owners granting access to their properties to the DePue Group, the Illinois Environmental Protection Agency (IEPA), and the United States Environmental Protection Agency (USEPA) and their representatives.

Sample Collection and Analysis Procedures

For each off-site property where access is allowed, a combination of composite and discrete (garden areas) soil samples will be collected. The sampling procedures will follow the guidance in the Superfund Lead-Contaminated Residential Sites Handbook (USEPA, 2003). A summary of the soil sampling is as follows:

Residential Property	Soil Samples
Lot with total yard surface area less than or equal to 5,000 square feet with no side yard or a side yard that is less than 1/3 of the total yard area	Front Yard – five-point composite: samples from each of the following depth intervals 0-1", 1-6", 6-12", 12-18", and 18-24". Back Yard – as above.
Lot with total yard surface area less than or equal to 5,000 square feet and a side yard that is approximately 1/3 of the total yard area	Front Yard – five-point composite: samples from each of the following depth intervals 0-1", 1-6", 6-12", 12-18", and 18-24". Back Yard – as above. Side Yard – as above.
Lot with total yard surface area greater than 5,000 square feet	Divide the yard into four equal quadrants. Five-point composite from each of the four quadrants from the depth intervals indicated above.
Lot greater than 1-acre	Divide into one-quarter-acre sections and sample as outlined above.
Drip zones	One four-point composite from the depth intervals indicated above. One aliquot will be obtained from each side of the house being sampled. Each aliquot will be collected from between 6 and 30 inches from the exterior wall of the home.
Downspout area (if present)	One four to five-point composite from the depth intervals indicated above. One aliquot will be obtained from each downspout area of the house being sampled.
Bare and Play Areas	Obtain composite samples from play areas within each portion of a property (e.g., back yard, front yard, side yard) from 0-1", 1-6", 6-12", 12-18", and 18-24". Two to five aliquots will make up a play area composite, depending on the number of play areas within a given portion of the property. Separate composite samples will be obtained for bare areas in the same manner as play areas. A final determination of the sampling requirements for these areas will be determined in the field in consultation with IEPA and/or their representatives.

Residential Property	Soil Samples
Garden Area	One discrete soil sample from each of the following depth intervals 0-6", 6-12", 12-18", and 18-24" for every 100 square feet of garden area. If raised garden beds are encountered, sampling will continue until the top 12 inches of native soil is sampled or to a depth of 2 feet below normal ground surface, whichever is less.
Ecological Habitat Areas	As outlined in Section 7.4.4 of the Design Study.

Note:
During the Pilot Study, the soil samples will be analyzed to 24 inches below ground surface (bgs) and deeper samples will be analyzed on a case-by-case basis (e.g., if visible plant-related material is observed at 24 inches bgs). The deeper samples will be obtained from the native material underlying the visible plant-related material. During the Design Study, initially, soil samples from the first 12 inches will be analyzed. If human health constituents of potential concern (HCOPCs) are detected greater than bright-line criteria in the first 12 inches, or if potential plant-related material is observed at 12 inches, the deeper samples will be analyzed.

Materials to be composited will be from the same depth profiles. The five aliquots of each composite sample from a yard area will be collected away from drip zones and away from influences of other possible sources (e.g., painted surface, burn areas, and debris piles). The specific procedures that will be used to homogenize, composite, subsample, split, and archive the soil samples are described in the soil sampling SOP included in Appendix A.

Detailed information regarding the number of samples (including QA/QC samples) and the analytical parameters are presented in Table 1 – Estimated Quantity of Environmental and Quality Control Samples.

Soil Sieving

To evaluate if the lead concentration in the fine soil fraction is more representative of potential exposure to lead in soil from ingestion, both total and fine fraction soil samples will be obtained and analyzed for lead during the Pilot Study. Approximately 20% (determined randomly) of the soil samples obtained from the 0 to 1-inch and 1 to 6-inch depth intervals will be analyzed for the fine fraction by drying the samples (if necessary), passing the soil through a No. 60 (250 micrometer) sieve, and collecting and analyzing the sieved soil. As presented in the Lead Guidance (USEPA, 2003), if paint chips are present in the soil, they will be included in the fine fraction sample by breaking up the paint chips and forcing the chips through the sieve. Both the total and fine (sieved) soil samples will be analyzed for lead by CLP and XRF methods.

Field Data Procedures

Information from each sample location will be entered into the field notebook, including geospatial location, land use, and physical description of the sample matrix (i.e., color, grain size, moisture content, presence/type of debris, and/or anthropogenic materials). Photographs will also be taken at each property that depicts each sample location. A GPS unit will be used to record each subsample location. The GPS unit will be a hand-held unit with a positional accuracy of 1 to 5 meters, with differential GPS (DGPS) corrections. In addition, written

descriptions of each individual sample location will be entered into the field notebook, along with appropriate distances to prominent landmarks.

Sample Archiving Procedures

The composite sampling procedures involve homogenizing each individual sample, obtaining a subsample from the homogenized sample for compositing, and splitting and archiving the remainder of the homogenized individual sample. The specific procedures that will be used to homogenize, composite, subsample, split, and archive the soil samples are described in the soil sampling procedures SOP (Appendix A). After field XRF analyses, the remainder of the XRF sample will also be achieved. Archived samples will be organized for future access and housed in storage in a secure location for up to six months.

3 Analytical Methodology

3.1 XRF Methodology

XRF analysis will be conducted using a Niton FXL 950 portable bench top-style analyzer by Thermo Scientific. The XRF will be set up at a fixed location and the same type of unit will be used throughout the duration of the investigation. Target XRF analytes for the Pilot Study include antimony, arsenic, barium, cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, thallium, and zinc. Target analytes for the Design Study will be determined based on the results of the Pilot Study.

XRF method details are presented in Appendix B. Appendix B also includes the technical guidelines supplied by the manufacturer and USEPA Method 6200 (2007).

3.2 Analytical Laboratory Methodology

Laboratory analyses for soils from the residential properties during the Pilot Study will include the HCOPCs antimony, arsenic, barium, cadmium, cobalt, copper, iron, lead, manganese, mercury, thallium, and zinc. Total chromium and hexavalent chromium will be analyzed at select locations in OU3, as outlined in the Pilot and Design Studies to determine if chromium is an HCOPC for residential properties. If it is determined that total chromium is an HCOPC, total chromium will also be analyzed at each Pilot Study and Design Study property. Soil pH will also be analyzed.

The HCOPCs for the Design Study will be determined based on the results of the Pilot Study. The Design Study sampling will include residential, residential-like, and special use areas. Ecological habitat areas will also be sampled during the Design Study. Laboratory analysis for ecological habitat areas will include the target analyte list (TAL) metals/cyanide with the exception of the essential nutrients calcium, magnesium, potassium, and sodium. Exchangeable metals, cation exchange capacity, total organic carbon, and particle size will also be analyzed in the ecological habitat areas.

The metals (excluding hexavalent chromium) analytes will be analyzed using Contract Laboratory Program (CLP) Method ISM01.3 or the most updated CLP Method. Stage 3 validation will be performed on the first 10 data packages and 1 in every 20 data packages, thereafter and a Stage 2A validation will be completed for the remaining data packages. Soil pH will be analyzed using SW-846 Method 9045. Hexavalent chromium will be analyzed using SW-846 Method 7196, total organic carbon will be analyzed by ASTM D4129, cation exchange capacity by SW-846 9081, and particle size by ASTM D422. Exchangeable metals will be analyzed using a neutral salt extraction using calcium nitrate and SW-846 Methods 6010/6020/7471.

4 Sample Designation System

If a macrocore sampler with an acetate liner is used to obtain samples, the liner will be clearly labeled prior to transport to the sample processing area. The label will include the property identification number (e.g., 52), the identification of the composite group or discrete sample associated with the sample (e.g., COMP 1 or Discrete 1) and sequential boring number for the property (e.g., 5). The identification of the composite group and the associated portion of a property will be recorded in the field notebook. An example label for an acetate liner obtained from property 52, composite group 3, and the fifth boring advanced on property 52 is: 52-COMP3-5. If a hand auger or split spoon sampler is used, the soils recovered from each sample interval (0- to 1-inch, 1-to 6-inch, 6- to 12-inch, 12- to 18-inch, and 18 to 24 inches) will be placed into separate gallon size self-sealing bags that are labeled as outlined above with the addition of the sample depth interval (e.g., 0-1).

The soil and quality assurance/quality control (QA/QC) samples will each be assigned a unique sample name and sample identification number. The sample name will be used on sample labels, chain of custody sheets, and field logbooks. For composite soil samples, the sample name will begin with the OU, followed by two letters indicating the sample type (e.g., SS for soil), two to three digits indicating the property identification, "COMP" to indicate a composite sample followed by the composite sample number (e.g., COMP1), followed by the sample depth in inches within parentheses. An example sample name for a composite soil sample obtained from 6 to 12 inches from composite area 3 from property 52 located in OU4 is: OU4-SS-52-COMP3 (6-12). Soil samples that are sieved for fine fraction lead analysis will be identified with the prefix "SV" at the end of the sample name.

For discrete samples, the sample name will be the same as above with the exception that the composite area will be replaced with the discrete sample number. An example sample name for the 3rd discrete soil sample obtained from 6 to 12 inches from property 52 located in OU4 is: OU4-SS-52-03(6-12).

Additional sample volumes collected for matrix spike (MS) and matrix spike duplicate (MSD) analysis will be noted on the chain-of-custody forms. Rinse blanks will use the same coding scheme noted above substituting the location code with the prefix "RB", the rinse sample number, and the date. An example sample name for the first rinse blank sample obtained on August 14, 2013 is: OU4-RBSS-01-081413. Field duplicates will be labeled as ordinary field samples with a unique sample name number and will be submitted to the laboratory as "blind" samples.

An eight-digit sample identification number will be assigned to each sample. The first four digits will identify the year, and the next four numbers will be a unique sequential identifier for each sample. An example sample identification number for a sample collected in 2013 is 20130035.

5 Sample Handling and Documentation

5.1 Sample Containers and Preservation

Appropriate sample containers, preservation methods, and laboratory holding times for soil samples are presented in Table 1 of the site-wide QAPP (Golder, 1999b). The analytical laboratory will supply appropriate sample containers in sealed cartons, as well as sample labels. The field personnel will be responsible for properly labeling containers and preserving samples (as appropriate). Sample handling, packing, and shipping procedures are described in the SOP provided in Appendix C of this FSP.

5.2 Sample Handling, Packing, and Shipping Requirements

Sample custody seals and packing materials for filled sample containers will be provided by the analytical laboratory. The filled, labeled, and sealed containers will be placed on ice and carefully packed in a cooler to minimize the possibility of container breakage.

All samples will be packaged by the field personnel and transported as low-concentration environmental samples. The packaged samples will be shipped via express overnight carrier to the laboratory. General procedures for handling, packing, and shipping environmental samples are included in Appendix C of this FSP.

5.3 Documentation

Field personnel will document field sampling, field analysis, and sample chain-of-custody (COC). This documentation constitutes a record that allows reconstruction of field events to aid in the data review and interpretation process. All documents, records, and information relating to the performance of the fieldwork will be retained in the project file.

The various forms of documentation to be maintained throughout the off-site soils investigations include:

- Daily Production Documentation – A field notebook consisting of a waterproof, bound notebook containing a record of activities performed for each sampling team.
- Sampling Information – Notes will be made regarding the location of sampling, physical observations, sample depths, and weather conditions.
- Sample Chain-of-Custody – COC forms will provide the record of responsibility for sample collection, transport, and submittal to the laboratory. COC forms will be filled out at each sampling location, at a group of sampling locations, or at the end of each day of sampling by the field personnel designated to be responsible for sample custody. In the event that the samples are relinquished by the designated sampling person to other sampling or field personnel, the COC form will be signed and dated by the appropriate personnel to document the sample transfer. The original COC form will accompany the samples to the laboratory, and copies will be forwarded to the project files. Persons will have custody of samples when the samples are in their physical possession, in their view after being in their possession, or in their physical possession and secured so they cannot be tampered with. In addition, when samples are secured in a restricted area accessible only to authorized personnel, they will be deemed to be in the custody of such authorized personnel.

- Field Equipment, Calibration, and Maintenance Logs – To document the calibration and maintenance of field instrumentation, calibration and maintenance logs will be maintained for each piece of field equipment that is not factory-calibrated.

5.4 Management of Excess Soils

Excess soil generated as a result of sampling activities will be placed back into the sample boreholes or placed in the Corrective Action Management Unit (CAMU) in OU3. The original sod from the borehole will be replaced when possible, and the borehole will be filled to land surface with clean topsoil and tamped down to preclude leaving holes.

6 Equipment Cleaning and Decontamination Procedures

6.1 General

The field equipment cleaning and decontamination procedures will generally follow the discussion provided in the Golder (1999a) site-wide FSP (Section 4.11: Decontamination of Drilling and Sampling Equipment, and the ENVIRON Site-Wide FSP Addendum (ENVIRON, 2006). Specifically, soil-sampling equipment, such as split spoons, macrocore samplers, mixing bowls, and spatulas will be decontaminated prior to collection of samples. The necessary decontamination procedures for sampling equipment are listed below:

- Tap water rinse,
- Wash/scrub with non-phosphate detergent and tap water,
- Rinse with tap water,
- Rinse with deionized or distilled water, and
- Air dry or blot off with clean white paper tower.

A detailed description of the procedures to be followed for decontaminating the field equipment is provided in Appendix D to this FSP.

6.2 Management of Derived Waste

Disposable equipment and debris, such as health and safety equipment, plastic sheeting, sampling equipment, and other equipment not reused in the investigation will be collected in plastic bags and disposed of as general refuse. Excess soils from the sample compositing and XRF analyses will be place into the CAMU. The waste materials will be disposed of by the DePue Group in accordance with applicable regulations.

Field sampling equipment will be decontaminated by following the procedures outlined in Appendix D to this FSP. Consistent with the existing site-wide FSP and Addenda, decontamination rinsate may be discharged directly to ground surface in OU3, as approved previous by IEPA. Decontamination rinsate will not be discharged to the ground surface within OU4.

7 Quality Assurance/Quality Control

This section summarizes the QA/QC requirements for field investigation activities associated with the off-site soils investigations. Additional information regarding the QA/QC procedures is presented in the existing site-wide QAPP (Golder, 1999b), and Addenda (ENVIRON, 2007), as amended by the QAPP Addendum (ENVIRON, 2013).

7.1 Field Instrumentation Calibration and Preventative Maintenance

Field personnel will be responsible for assuring that a master calibration/maintenance log is maintained for each measuring device. Each log will include, at a minimum (where applicable):

- Name of device and/or instrument calibrated (e.g., Niton FXL);
- Device/instrument serial/ID number;
- Frequency of calibration;
- Date(s) of calibration(s);
- Results of calibration(s); and
- Name of person(s) performing calibration(s).

Equipment to be used each day shall be calibrated prior to the commencement of activities or as suggested by the manufacturer.

7.2 QA/QC Sample Collection

The frequency of QA/QC field sample collection is provided in Table 1. This estimate is based on the QA/QC sample collection frequency discussed in the site-wide QAPP and QAPP Addendum. Guidance on the collection of the QA/QC samples is presented below.

Rinse Blanks

Rinse blanks will be prepared in the field by pouring laboratory-supplied analyte-free water over decontaminated sampling equipment and then laboratory-supplied sample bottles to check that the decontamination procedure has been adequately performed and that the equipment will not lead to cross contamination of samples. The intent is for the water making up the blank to follow the same path, and therefore, come in contact with the same equipment as the samples. Consistent with the site-wide QAPP, rinse blanks will be collected at a rate of once per day, and shall not exceed 5% of the total number of samples. Rinse blanks will be performed on decontaminated soil sampling equipment and other equipment, such as bowls or pans used to homogenize samples. Rinse blanks will be collected at the beginning of the day before the sampling event and must accompany the samples collected that day.

Duplicate Samples

Duplicate samples will be collected for both XRF analysis and laboratory analysis. Data from the duplicate samples will be used to evaluate the reproducibility of the sampling technique used. Five percent (5%) (i.e., one for every 20 samples) of each matrix will be duplicated. Duplicate samples will be collected using methods to maximize the compatibility of the samples.

For example, soil collected from a particular location will be thoroughly homogenized and then divided between the sample and duplicate sample laboratory containers.

Matrix Spike/Matrix Spike Duplicate

Triple sample volumes from designated sample locations will be collected in order to perform matrix spike/matrix spike duplicate (MS/MSD) analysis. Table 1 sets forth the frequency of collection for MS/MSD.

8 References

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BBL. 2005b. "QAPP Addendum." Prepared for the DePue Group.

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Golder. 1999b. "Appendix C: Quality Assurance Project Plan for Remedial Investigation Phase I Soil and Groundwater." Prepared for the DePue Group.

Golder. 1999c. "Appendix B: Health and Safety Plan for Remedial Investigation Phase I Soil and Groundwater." Prepared for the DePue Group.

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Tables

TABLE 1
Estimated Quantity of Environmental and Quality Control Samples
DePue Site
DePue, Illinois

Parameter	Estimated Environmental Sample Quality	Field QC Analysis						Laboratory QC Sample						Total
		Trip Blank		Rinse Blank		Field Duplicate		Matrix Spike		Matrix Spike Duplicate		Lab Duplicate		
		Frequency	Number	Frequency	Number	Frequency	Number	Frequency	Number	Frequency	Number	Frequency	Number	
Soil														
Metals (ISM01.3)	TBD	NA	--	1/day	TBD	1/20	TBD	1/20	TBD	NA	--	1/20	TBD	TBD
Metals (SW-846 6200)	TBD	NA	--	1/day	TBD	1/day or 1/20	TBD	1/20	TBD	NA	--	1/20	TBD	TBD
pH (SW-846 9045)	TBD	NA	--	NA	--	NA	TBD	NA	--	NA	--	1/20	TBD	TBD
Hexavalent Chromium (SW-846 7196)	16	NA	--	1/day	TBD	1/20	1	1/20	1	1/20	1	1/20	1	TBD
Total Organic Carbon (ASTM D4129)	TBD	NA	--	1/day	TBD	1/20	1	1/20	1	1/20	1	1/20	1	TBD
Cation Exchange Capacity (SW-846 9081)	TBD	NA	--	NA	--	1/20	TBD	1/20	TBD	1/20	TBD	1/20	TBD	TBD
Particle Size (ASTM D422)	TBD	NA	--	NA	--	NA	--	NA	--	NA	--	NA	--	TBD

Notes:
1/day =One rinse blank per day or one per 20 samples, whichever is more frequent. Rinse blanks not required when dedicated sampling equipment is used.
- One precision sample analysis will be performed per day or one per 20 samples, whichever is more frequent. The relative percent difference acceptance criteria are outlined in section 7 of the QAPP.
NA = Not Applicable
QC =Quality Control
TBD = To Be Determined

Appendix A

Soil Sampling Standard Operating Procedures

Appendix A: Soil Sampling Standard Operating Procedures

Soil Sampling

The information in this Soil Sampling Standard Operating Procedure (SOP) describes the methods that will be used to collect soil samples at off-site properties as part of the Pilot Study or Design Study.

Materials

The following equipment and materials, as required, will be available during soil sampling:

- Personal protective equipment (PPE) (as required by the Health and Safety Plan (HASP);
- Cleaning and decontamination equipment (as specified in Appendix D of this FSP);
- Pin flags;
- Glass or stainless steel bowls, pans, and/or trays;
- Appropriate sample containers and forms;
- Insulated coolers with ice;
- Hand-operated soil sampling equipment (split-spoon or macrocore sampler);
- Stainless steel bucket auger;
- Brass push rod;
- Stainless steel scoop;
- Spade (square-nosed);
- 6-Foot ruler and 100-foot measuring tape;
- Stainless steel spatulas;
- A digital camera;
- Hand-held global position system (GPS) surveying unit; and
- Field logbook.

Procedures

The following procedures will be employed to collect soil samples:

1. Don PPE (as required by the HASP).
2. Identify proposed sample location from the Work Plan.
3. Verify that the proposed sample locations are not located in the immediate vicinity of underground utilities. (Note: Utility clearance will be requested at least two working days before sampling is scheduled to begin.)

4. For yard areas, mark each individual sample location for the five-point composite sample using pin flags. Note that sample locations should be outside of the drip zones and away from influences of other possible sources. For drip zone samples, up to a four-point composite sample (one from each side of the house). Composite samples will be obtained from play areas within each portion of a property (e.g., back yard, front yard, side yard) from 0-1", 1-6", 6-12", 12-18", and 18-24". Two to five aliquots will make up a play area composite, depending on the number of play areas within a given portion of a property. Separate composite samples will be obtained for bare areas in the same manner as play areas. A final determination of the sampling requirements for these areas will be determined in the field in consultation with IEPA and/or their representatives. For garden areas, a discrete sample will be obtained for every 100-square feet of garden area. For downspout discharge areas, up to a five-point composite sample will be obtained from the house.
5. Measure and record the sample locations using a hand-held GPS unit. In addition, provide written descriptions of sample locations with approximate distances to prominent landmarks. Note this information in the field logbook.
6. If the sample location is a vegetated area, the vegetation should be removed prior to collecting the soil sample(s).
7. Using a hand-auger, split-spoon sampler or macrocore samples (with an acetate liner), advance with a straight, vertical entry into the soil, so as to secure a reasonably representative sample. Measure and record the depth of soil penetrated. Total depth should be a minimum of 18 inches and maximum of 24 inches. If required for additional sample mass, advance a second sampler immediately adjacent to the first sampler.
8. If a macrocore sampler is used, remove liner, label, and place in temporary transport container. If a split spoon or hand auger is used, place each depth interval to be analyzed (0- to 1-inch, 1-to 6-inch, 6- to 12-inch, 12- to 18-inch, and 18- to 24 inches) into separate gallon size self-sealing bags that are labeled as outlined in Section 4 of the FSP.
9. If necessary to achieve required sample mass, supplement the 0- to 1-inch sample with additional soil, collected using a stainless steel trowel or spade (e.g., square-nosed spade to lift sod) in an approximate one foot square at the sample location. Place in a gallon size self-sealing plastic bag, label, and place in temporary transport container.
10. Fill the remaining void with hand-compacted, clean topsoil. Replace displaced grass, if possible.
11. Repeat steps 5 through 10 at the remaining sample locations for the composite samples.
12. Transfer samples to field office/temporary field laboratory.
13. Remove the samples and place on a stainless steel tray.
14. With a pre-cleaned spatula or knife, remove all excess soil from the outside of the sample to avoid cross-contamination over the sample depth.
15. Cut open liners and place the sample onto a stainless steel tray.
16. Measure, photograph, and describe each soil core with respect to color, grain size, moisture content, and presence of debris/anthropogenic materials.

17. Separate the sample into the following depth increments: 0- to1-inch; 1- to 6-inch; 6- to12-inch; 12- to 18-inch, and 18- to 24-inch.
18. Remove large rocks or other debris (e.g., twigs, grass, rocks, and roots) from each sample.
19. If the moisture content is greater than 20 percent and/or if soil moisture and cohesion prevent homogenization, the sample will be dried by placing the sample in an oven for 2 to 4 hours at a temperature less than 150° C or air dried overnight. If necessary, due to soil characteristics (e.g., cohesiveness or coarseness), grind the sample using a mortar and pestle.
20. Thoroughly homogenize each sample using a stainless steel spatula in a stainless steel/glass pan or bowl. If mixed in a pan, mix each quarter of the pan separately and then together in the middle of the pan. If mixed in a bowl, stir in a circular fashion occasionally turning the material over.
21. Once homogenized, evenly spread the sample in a rectangular steel pan/tray. Then using a scoop, take multiple scoops in evenly spaced swaths along the short axis of the spread sample until the scoop is full. The scoop represents a subsample of equal volume. Place full scoop in stainless steel/glass bowl or pan. Repeat for each sample that is part of the composite group.
22. Repeat Steps 18, 19, 20, and 21 for all appropriate depth increment samples to be composited. Place remainder of individual samples into appropriate sample jar or baggie for on-site storage/future field or laboratory analysis. (Note: If an individual sample is selected for field analysis, the stored sample will be re-homogenized [in case of settling], spread in a rectangular pan/tray, and then split by dividing the spread sample into an equal amount of increments and collecting alternate increments with a scoop until half the sample is segregated from the other half remaining on the pan/tray. One half will be used for field analysis and the other half will be placed into an appropriate sample jar or baggie for on-site storage/potential future laboratory analysis.)
23. Combine equal sample volumes from like depth increments from the individual samples to be composited into the stainless steel/glass bowl or pan, homogenize the composite sample as per Step 20.
24. Once homogenized, spread composite sample as per Step 21, then split by dividing the spread sample into an equal number of increments and collecting alternate increments with a scoop until half the sample is segregated from the other half remaining on the pan/tray. One half will be used for XRF and laboratory analysis and the other half will be placed into an appropriate sample jar for on-site storage. The same XRF sample cup or plastic baggie will be submitted to the laboratory for analysis
25. Repeat Steps 13 to 24 for all depth increments/sample locations.
26. The samples selected for fine fraction of lead analysis will be prepared by passing an aliquot of the combined, homogenized sample prepared above through a #60 sieve (stainless steel or nylon). The sieve will be agitated manually or with a mechanical shaker. The material passing through the sieve will be divided into two aliquots for XRF/laboratory analysis of lead and sample archiving.

27. The samples may be further divided (using the technique described above), as appropriate, for proper containerizing, preserving, and shipping for laboratory analysis. In addition, blind duplicate samples or MS/MSD samples may also be prepared, consistent with the procedures outlined in the QAPP.
28. Label, handle, pack, and ship the samples in accordance with Appendix C to the FSP.

References:

ASTM D 6051-96 (Reapproved 2006): Standard Guide for Composite Sampling and Field Subsampling for Environmental Waste Management Activities.

Appendix B

Standard Operating Procedures for Metals Analysis Using Field Portable X-Ray Fluorescence Analyzers

Appendix B: Standard Operating Procedures for Metals Analysis Using Field Portable X-Ray Fluorescence Analyzers

Scope and Application

This Standard Operating Procedure (SOP) provides general guidance for the operation of XRF instruments for the analysis of inorganic metals in soil. The SOP describes general principles, materials, and methodology used for intrusive XRF and technical information from the manufacturer for the specific equipment that will be employed. Attached to this SOP is the USEPA SW-846 Method 6200 (2007) Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment (Attachment 1), which will be utilized as the basis for QA/QC procedures and the Niton FXL User's Guide (Attachment 2).

XRF analyses will be conducted on the homogenized soil samples. As described in USEPA Method 6200, additional enhancements to the sample preparation (i.e., drying, grinding) may also be required to achieve lower detection limits and/or to decrease soil heterogeneity. Procedures will be adjusted, as necessary, to accommodate additional sample preparation.

Materials

The following materials, as required, will be available during XRF soils analysis:

- Personal protective equipment (PPE) (as required by the Health and Safety Plan [HASP]);
- Cleaning and decontamination equipment (as specified in Appendix D);
- Analyzer unit with data acquisition, processing, display, and computer interface;
- Computer and printer;
- Lithium-ion batteries;
- Battery charging system;
- Polyethylene sample cups: 31 millimeters (mm) to 40 mm in diameter with collar, or equivalent (as specified for the XRF instrument);
- X-ray window film : Mylar™, Kapton™, polypropylene, or equivalent 2.5 or 6.0 micrometers (µm) thick;
- Moisture content meter (e.g., General® Digital (DSMM500) or equivalent;
- Mortar and pestle;
- Equipment blank samples (e.g., pure silica dioxide);
- Method blank samples (e.g., pure silica sand);
- Calibration standard (e.g., standard reference material);
- Drying oven (convection or toaster oven);
- Thermometer;
- Aluminum or stainless steel bowl and tray;

- Appropriate containers, labels, and forms;
- Field notebook;
- Camera and film (or digital camera);
- Field equipment logbook;
- Property analysis results notebook; and
- Instrument operation manual.

Procedures

The following procedures will be used to perform the XRF analysis:

Sample Preparation

The samples will be prepared for XRF analysis as summarized in Appendix A: Soil Sampling Procedures.

Quality Assurance/Quality Control

- Follow quality assurance/quality control (QA/QC) procedures as specified in the QAPP Addendum and in accordance with manufacturer instructions and USEPA Method 6200.
- Perform energy calibration check sample at least twice daily. This test is typically done automatically within the equipment during the startup or standardization procedures using a pure element standard (e.g., Pb, Fe, Cu). Appropriate energy calibration information (e.g., date, time, etc.) will be recorded within the field equipment logbook.
- Analyze equipment blank at a specified frequency (e.g., 1 per 20 samples) using pure silicon dioxide. Record date, time, and result within the field equipment logbook.
- Analyze method blank at specified frequency (e.g., 1 per 20 samples) using clean silica sand, which will undergo the same sample preparation procedures as a field sample to ensure that there is no cross-contamination during the sample preparation procedure. Record date, time, and result within the field equipment logbook.
- Analyze precision measurement (e.g., test relative standard deviation [RSD] amongst seven replicates) at a specified frequency (e.g., once per day) using field samples. The selected field samples (when possible) will exhibit XRF-targeted metals concentration ranges with at least one sample with target analyte concentrations near the bright-line criteria. If the RSD value exceeds 20 percent (30 percent for chromium), then an increase in the sample count time is necessary. The sample count time will be increased by 30-second increments until an acceptable RSD is achieved. Record date, time, and result within the field equipment logbook.
- Average site-specific method detection limits (MDLs) and practical quantitation limits (PQLs) will be generated using results from replicate (7) analyses of the low concentration Standard Reference Material (SRM) samples discussed below. The method detection limit will be defined as 3 times the standard deviation of the results and the method quantitation limit will be defined as 10 times the standard deviation of the same results.

Calibration Verification Check

Multiple SRMs will be used for the calibration verification check of the XRF instrument. National Institute of Standards and Technology (NIST) SRM 2710a (Montana I Soil) and SRM (Trace Elements in Soil) will be used for the calibration verification checks. NIST SRM 2710a contains certified values for the Human Health Constituents of Potential Concern (HCOPCs) except chromium and thallium, which are NIST reference concentrations. NIST SRM 2586 contains certified values for arsenic, cadmium, chromium, and lead with the certified values for arsenic and lead at concentrations near their respective potential bright-line criteria. The table below summarizes the HCOPC and their respective bright-line criteria and the respective concentration ranges for NIST SRMs 2710a and 2586.

Chemical	Final Residential Bright-Line Criteria	NIST SRM[1]			
		2586		2710a	
Antimony	3.1E+01	--		5.25E+01	C
Arsenic	TBD	8.7E+00	C	1.54E+03	C
Barium	1.4E+04	4.13E+02	R	7.92E+02	C
Cadmium	7.0E+01	2.71E+00	C	1.23E+01	C
Chromium (III)[2]	1.2E+05	3.01E+02	C	2.3E+01	R
Chromium (VI)[2]	2.3E+02	3.01E+02	C	2.3E+01	R
Cobalt	2.3E+01	--		5.99E+00	C
Copper	3.1E+03	--		3.42E+03	C
Iron	5.5E+04	5.161E+04	R	4.32E+04	C
Lead	TBD	4.32E+02	C	5.52E+03	C
Manganese	1.8E+03	1.0E+03	R	2.14E+03	C
Mercury	2.3E+01	3.67E-01	R	9.88E+00	C
Thallium	6.3E+00	--		1.52E+00	R
Zinc	2.3E+04	3.52E+02	R	4.18E+03	C

Key:

-- = Not Present in SRM
C = NIST Certified Concentration Value
R = NIST Reference Concentration Value
TBD = to be determined

Notes:

1 = Standard Reference Materials. Data taken from www.nist.gov/srm
2 = SRMs do not delineate between different chromium valences, nor does XRF due to operating principles

Sample Analysis

- Don PPE equipment (as required by the HASP).
- Startup analyzer equipment (as per manufacturer's instructions) and allow 15 minutes for warm up.
- Check battery life. If low, then replace before proceeding.
- Set up instrument for soil testing for target analytes (as per manufacturer instructions). This will include entering target analytes, associated action limits, sample time, and sample identification number.
- Remove an aliquot of the soil from the sample jar and follow sample preparation procedure in Appendix A.
- Run soil sample according to specified target analytes and associated data quality objectives. Based on the potential interference amongst certain analytes (e.g., Pb and As), sample times will be determined based on the effectiveness of the XRF equipment and the level of resolution desired. Sample run time is inversely related to the square of the measurement error and detection limit and will be determined by analyzing the NIST standard 2586 four times at the instrument's maximum measurement time of approximately 300 seconds. The average run time required such that the measured result uncertainty for lead that is less than 5 percent from the standard value will be determined. This value will be rounded to the nearest 30 seconds to determine the run time. Based on the 2012 XRF Data Usability Study, the instrument default analysis time of either 120 to 180 seconds is likely appropriate. Once a run time is selected, it will be used for all samples for uniformity. If lower detection limits or lower uncertainty are needed, then analysis times can be increased. However, due to the squared relation between measurement error and analysis time, there is a point of diminishing returns where additional sample time does not appreciably increase confidence or detection ability.
- Once the desired resolution has been met for the target analytes, end sampling run.
- Remove sample cup or baggie from analyzer and submit the sample to the laboratory for analysis.

Data and Reporting Procedures

- Upon completion of sample analysis, export all readings and spectrum data for the day to connected portable computer.
- Save data files according to project database requirements.
- Using Microsoft® Access, import electronic data files into the project database (e.g., EQuIS) at the end of the work shift.
- Upload data to ENVIRON server.
- Follow appropriate project requirements for any additional data deliverables (e.g., hardcopies for agencies and property owners, e-mail to project manager, etc.)

Data Evaluation

Laboratory data will be compared to XRF data according to guidance in USEPA Method 6200 (2007 version). Results will be will be evaluated with a log-transformed linear least squares regression analysis. In addition, inferential statistics will be run on the data so that the determination can be made if the XRF data qualifies as definitive. The inferential statistics that will be used will either be a Two Sample Paired T-test (for data determined to be normal or log-normal) of the Wilcoxon Signed Rank test (for data determined to neither normal nor log-normal). These tests will be run at a 99-percent confidence level to determine if the data statistically equivalent.

Attachment 1

USEPA Method 6200 (2007)

METHOD 6200

FIELD PORTABLE X-RAY FLUORESCENCE SPECTROMETRY FOR THE DETERMINATION OF ELEMENTAL CONCENTRATIONS IN SOIL AND SEDIMENT

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the in situ and intrusive analysis of the 26 analytes listed below for soil and sediment samples. Some common elements are not listed in this method because they are considered "light" elements that cannot be detected by field portable x-ray fluorescence (FPXRF). These light elements are: lithium, beryllium, sodium, magnesium, aluminum, silicon, and phosphorus. Most of the analytes listed below are of environmental concern, while a few others have interference effects or change the elemental composition of the matrix, affecting quantitation of the analytes of interest. Generally elements of atomic number 16 or greater can be detected and quantitated by FPXRF. The following RCRA analytes have been determined by this method:

Analytes	CAS Registry No.
Antimony (Sb)	7440-36-0
Arsenic (As)	7440-38-0
Barium (Ba)	7440-39-3
Cadmium (Cd)	7440-43-9
Chromium (Cr)	7440-47-3
Cobalt (Co)	7440-48-4
Copper (Cu)	7440-50-8
Lead (Pb)	7439-92-1
Mercury (Hg)	7439-97-6
Nickel (Ni)	7440-02-0
Selenium (Se)	7782-49-2
Silver (Ag)	7440-22-4
Thallium (Tl)	7440-28-0
Tin (Sn)	7440-31-5

Analytes	CAS Registry No.
Vanadium (V)	7440-62-2
Zinc (Zn)	7440-66-6

In addition, the following non-RCRA analytes have been determined by this method:

Analytes	CAS Registry No.
Calcium (Ca)	7440-70-2
Iron (Fe)	7439-89-6
Manganese (Mn)	7439-96-5
Molybdenum (Mo)	7439-93-7
Potassium (K)	7440-09-7
Rubidium (Rb)	7440-17-7
Strontium (Sr)	7440-24-6
Thorium (Th)	7440-29-1
Titanium (Ti)	7440-32-6
Zirconium (Zr)	7440-67-7

1.2 This method is a screening method to be used with confirmatory analysis using other techniques (e.g., flame atomic absorption spectrometry (FLAA), graphite furnance atomic absorption spectrometry (GFAA), inductively coupled plasma-atomic emission spectrometry, (ICP-AES), or inductively coupled plasma-mass spectrometry, (ICP-MS)). This method's main strength is that it is a rapid field screening procedure. The method's lower limits of detection are typically above the toxicity characteristic regulatory level for most RCRA analytes. However, when the obtainable values for precision, accuracy, and laboratory-established sensitivity of this method meet project-specific data quality objectives (DQOs), FPXRF is a fast, powerful, cost effective technology for site characterization.

1.3 The method sensitivity or lower limit of detection depends on several factors, including the analyte of interest, the type of detector used, the type of excitation source, the strength of the excitation source, count times used to irradiate the sample, physical matrix effects, chemical matrix effects, and interelement spectral interferences. Example lower limits of detection for analytes of interest in environmental applications are shown in Table 1. These limits apply to a clean spiked matrix of quartz sand (silicon dioxide) free of interelement spectral interferences using long (100 -600 second) count times. These sensitivity values are given for guidance only and may not always be achievable, since they will vary depending on the sample matrix, which instrument is used, and operating conditions. A discussion of performance-based sensitivity is presented in Sec. 9.6.

1.4 Analysts should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.5 Use of this method is restricted to use by, or under supervision of, personnel appropriately experienced and trained in the use and operation of an XRF instrument. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 The FPXRF technologies described in this method use either sealed radioisotope sources or x-ray tubes to irradiate samples with x-rays. When a sample is irradiated with x-rays, the source x-rays may undergo either scattering or absorption by sample atoms. This latter process is known as the photoelectric effect. When an atom absorbs the source x-rays, the incident radiation dislodges electrons from the innermost shells of the atom, creating vacancies. The electron vacancies are filled by electrons cascading in from outer electron shells. Electrons in outer shells have higher energy states than inner shell electrons, and the outer shell electrons give off energy as they cascade down into the inner shell vacancies. This rearrangement of electrons results in emission of x-rays characteristic of the given atom. The emission of x-rays, in this manner, is termed x-ray fluorescence.

Three electron shells are generally involved in emission of x-rays during FPXRF analysis of environmental samples. The three electron shells include the K, L, and M shells. A typical emission pattern, also called an emission spectrum, for a given metal has multiple intensity peaks generated from the emission of K, L, or M shell electrons. The most commonly measured x-ray emissions are from the K and L shells; only metals with an atomic number greater than 57 have measurable M shell emissions.

Each characteristic x-ray line is defined with the letter K, L, or M, which signifies which shell had the original vacancy and by a subscript alpha (α), beta (β), or gamma (γ) etc., which indicates the higher shell from which electrons fell to fill the vacancy and produce the x-ray. For example, a K_α line is produced by a vacancy in the K shell filled by an L shell electron, whereas a K_β line is produced by a vacancy in the K shell filled by an M shell electron. The K_α transition is on average 6 to 7 times more probable than the K_β transition; therefore, the K_α line is approximately 7 times more intense than the K_β line for a given element, making the K_α line the choice for quantitation purposes.

The K lines for a given element are the most energetic lines and are the preferred lines for analysis. For a given atom, the x-rays emitted from L transitions are always less energetic than those emitted from K transitions. Unlike the K lines, the main L emission lines (L_α and L_β) for an element are of nearly equal intensity. The choice of one or the other depends on what interfering element lines might be present. The L emission lines are useful for analyses involving elements of atomic number (Z) 58 (cerium) through 92 (uranium).

An x-ray source can excite characteristic x-rays from an element only if the source energy is greater than the absorption edge energy for the particular line group of the element, that is, the K absorption edge, L absorption edge, or M absorption edge energy. The absorption edge energy is somewhat greater than the corresponding line energy. Actually, the K absorption edge energy is approximately the sum of the K, L, and M line energies of the particular element, and the L absorption edge energy is approximately the sum of the L and M line energies. FPXRF is more sensitive to an element with an absorption edge energy close to but less than

the excitation energy of the source. For example, when using a cadmium-109 source, which has an excitation energy of 22.1 kiloelectron volts (keV), FPXRF would exhibit better sensitivity for zirconium which has a K line energy of 15.77 keV than to chromium, which has a K line energy of 5.41 keV.

2.2 Under this method, inorganic analytes of interest are identified and quantitated using a field portable energy-dispersive x-ray fluorescence spectrometer. Radiation from one or more radioisotope sources or an electrically excited x-ray tube is used to generate characteristic x-ray emissions from elements in a sample. Up to three sources may be used to irradiate a sample. Each source emits a specific set of primary x-rays that excite a corresponding range of elements in a sample. When more than one source can excite the element of interest, the source is selected according to its excitation efficiency for the element of interest.

For measurement, the sample is positioned in front of the probe window. This can be done in two manners using FPXRF instruments, specifically, in situ or intrusive. If operated in the in situ mode, the probe window is placed in direct contact with the soil surface to be analyzed. When an FPXRF instrument is operated in the intrusive mode, a soil or sediment sample must be collected, prepared, and placed in a sample cup. The sample cup is then placed on top of the window inside a protective cover for analysis.

Sample analysis is then initiated by exposing the sample to primary radiation from the source. Fluorescent and backscattered x-rays from the sample enter through the detector window and are converted into electric pulses in the detector. The detector in FPXRF instruments is usually either a solid-state detector or a gas-filled proportional counter. Within the detector, energies of the characteristic x-rays are converted into a train of electric pulses, the amplitudes of which are linearly proportional to the energy of the x-rays. An electronic multichannel analyzer (MCA) measures the pulse amplitudes, which is the basis of qualitative x-ray analysis. The number of counts at a given energy per unit of time is representative of the element concentration in a sample and is the basis for quantitative analysis. Most FPXRF instruments are menu-driven from software built into the units or from personal computers (PC).

The measurement time of each source is user-selectable. Shorter source measurement times (30 seconds) are generally used for initial screening and hot spot delineation, and longer measurement times (up to 300 seconds) are typically used to meet higher precision and accuracy requirements.

FPXRF instruments can be calibrated using the following methods: internally using fundamental parameters determined by the manufacturer, empirically based on site-specific calibration standards (SSCS), or based on Compton peak ratios. The Compton peak is produced by backscattering of the source radiation. Some FPXRF instruments can be calibrated using multiple methods.

3.0 DEFINITIONS

3.1 FPXRF -- Field portable x-ray fluorescence.

3.2 MCA -- Multichannel analyzer for measuring pulse amplitude.

3.3 SSCS -- Site-specific calibration standards.

3.4 FP -- Fundamental parameter.

3.5 ROI -- Region of interest.

3.6 SRM – Standard reference material; a standard containing certified amounts of metals in soil or sediment.

3.7 eV – Electron volt; a unit of energy equivalent to the amount of energy gained by an electron passing through a potential difference of one volt.

3.8 Refer to Chapter One, Chapter Three, and the manufacturer's instructions for other definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 The total method error for FPXRF analysis is defined as the square root of the sum of squares of both instrument precision and user- or application-related error. Generally, instrument precision is the least significant source of error in FPXRF analysis. User- or application-related error is generally more significant and varies with each site and method used. Some sources of interference can be minimized or controlled by the instrument operator, but others cannot. Common sources of user- or application-related error are discussed below.

4.2 Physical matrix effects result from variations in the physical character of the sample. These variations may include such parameters as particle size, uniformity, homogeneity, and surface condition. For example, if any analyte exists in the form of very fine particles in a coarser-grained matrix, the analyte's concentration measured by the FPXRF will vary depending on how fine particles are distributed within the coarser-grained matrix. If the fine particles "settle" to the bottom of the sample cup (i.e., against the cup window), the analyte concentration measurement will be higher than if the fine particles are not mixed in well and stay on top of the coarser-grained particles in the sample cup. One way to reduce such error is to grind and sieve all soil samples to a uniform particle size thus reducing sample-to-sample particle size variability. Homogeneity is always a concern when dealing with soil samples. Every effort should be made to thoroughly mix and homogenize soil samples before analysis. Field studies have shown heterogeneity of the sample generally has the largest impact on comparability with confirmatory samples.

4.3 Moisture content may affect the accuracy of analysis of soil and sediment sample analyses. When the moisture content is between 5 and 20 percent, the overall error from moisture may be minimal. However, moisture content may be a major source of error when analyzing samples of surface soil or sediment that are saturated with water. This error can be minimized by drying the samples in a convection or toaster oven. Microwave drying is not recommended because field studies have shown that microwave drying can increase variability between FPXRF data and confirmatory analysis and because metal fragments in the sample can cause arcing to occur in a microwave.

4.4 Inconsistent positioning of samples in front of the probe window is a potential source of error because the x-ray signal decreases as the distance from the radioactive source increases. This error is minimized by maintaining the same distance between the window and each sample. For the best results, the window of the probe should be in direct contact with the sample, which means that the sample should be flat and smooth to provide a good contact surface.

4.5 Chemical matrix effects result from differences in the concentrations of interfering elements. These effects occur as either spectral interferences (peak overlaps) or as x-ray absorption and enhancement phenomena. Both effects are common in soils contaminated with heavy metals. As examples of absorption and enhancement effects; iron (Fe) tends to absorb copper (Cu) x-rays, reducing the intensity of the Cu measured by the detector, while chromium (Cr) will be enhanced at the expense of Fe because the absorption edge of Cr is slightly lower in energy than the fluorescent peak of iron. The effects can be corrected mathematically through the use of fundamental parameter (FP) coefficients. The effects also can be compensated for using SSCS, which contain all the elements present on site that can interfere with one another.

4.6 When present in a sample, certain x-ray lines from different elements can be very close in energy and, therefore, can cause interference by producing a severely overlapped spectrum. The degree to which a detector can resolve the two different peaks depends on the energy resolution of the detector. If the energy difference between the two peaks in electron volts is less than the resolution of the detector in electron volts, then the detector will not be able to fully resolve the peaks.

The most common spectrum overlaps involve the K_β line of element Z-1 with the K_α line of element Z. This is called the K_α/K_β interference. Because the K_α:K_β intensity ratio for a given element usually is about 7:1, the interfering element, Z-1, must be present at large concentrations to cause a problem. Two examples of this type of spectral interference involve the presence of large concentrations of vanadium (V) when attempting to measure Cr or the presence of large concentrations of Fe when attempting to measure cobalt (Co). The V K_α and K_β energies are 4.95 and 5.43 keV, respectively, and the Cr K_α energy is 5.41 keV. The Fe K_α and K_β energies are 6.40 and 7.06 keV, respectively, and the Co K_α energy is 6.92 keV. The difference between the V K_β and Cr K_α energies is 20 eV, and the difference between the Fe K_β and the Co K_α energies is 140 eV. The resolution of the highest-resolution detectors in FPXRF instruments is 170 eV. Therefore, large amounts of V and Fe will interfere with quantitation of Cr or Co, respectively. The presence of Fe is a frequent problem because it is often found in soils at tens of thousands of parts per million (ppm).

4.7 Other interferences can arise from K/L, K/M, and L/M line overlaps, although these overlaps are less common. Examples of such overlap involve arsenic (As) K_α/lead (Pb) L_α and sulfur (S) K_α/Pb M_α. In the As/Pb case, Pb can be measured from the Pb L_β line, and As can be measured from either the As K_α or the As K_β line; in this way the interference can be corrected. If the As K_β line is used, sensitivity will be decreased by a factor of two to five times because it is a less intense line than the As K_α line. If the As K_α line is used in the presence of Pb, mathematical corrections within the instrument software can be used to subtract out the Pb interference. However, because of the limits of mathematical corrections, As concentrations cannot be efficiently calculated for samples with Pb:As ratios of 10:1 or more. This high ratio of Pb to As may result in reporting of a "nondetect" or a "less than" value (e.g., <300 ppm) for As, regardless of the actual concentration present.

No instrument can fully compensate for this interference. It is important for an operator to understand this limitation of FPXRF instruments and consult with the manufacturer of the FPXRF instrument to evaluate options to minimize this limitation. The operator's decision will be based on action levels for metals in soil established for the site, matrix effects, capabilities of the instrument, data quality objectives, and the ratio of lead to arsenic known to be present at the site. If a site is encountered that contains lead at concentrations greater than ten times the concentration of arsenic it is advisable that all critical soil samples be sent off site for confirmatory analysis using other techniques (e.g., flame atomic absorption spectrometry (FLAA), graphite furnance atomic absorption spectrometry (GFAA), inductively coupled plasma-

atomic emission spectrometry, (ICP-AES), or inductively coupled plasma-mass spectrometry, (ICP-MS)).

4.8 If SSCS are used to calibrate an FPXRF instrument, the samples collected must be representative of the site under investigation. Representative soil sampling ensures that a sample or group of samples accurately reflects the concentrations of the contaminants of concern at a given time and location. Analytical results for representative samples reflect variations in the presence and concentration ranges of contaminants throughout a site. Variables affecting sample representativeness include differences in soil type, contaminant concentration variability, sample collection and preparation variability, and analytical variability, all of which should be minimized as much as possible.

4.9 Soil physical and chemical effects may be corrected using SSCS that have been analyzed by inductively coupled plasma (ICP) or atomic absorption (AA) methods. However, a major source of error can be introduced if these samples are not representative of the site or if the analytical error is large. Another concern is the type of digestion procedure used to prepare the soil samples for the reference analysis. Analytical results for the confirmatory method will vary depending on whether a partial digestion procedure, such as Method 3050, or a total digestion procedure, such as Method 3052, is used. It is known that depending on the nature of the soil or sediment, Method 3050 will achieve differing extraction efficiencies for different analytes of interest. The confirmatory method should meet the project-specific data quality objectives (DQOs).

XRF measures the total concentration of an element; therefore, to achieve the greatest comparability of this method with the reference method (reduced bias), a total digestion procedure should be used for sample preparation. However, in the study used to generate the performance data for this method (see Table 8), the confirmatory method used was Method 3050, and the FPXRF data compared very well with regression correlation coefficients (r often exceeding 0.95, except for barium and chromium). The critical factor is that the digestion procedure and analytical reference method used should meet the DQOs of the project and match the method used for confirmation analysis.

4.10 Ambient temperature changes can affect the gain of the amplifiers producing instrument drift. Gain or drift is primarily a function of the electronics (amplifier or preamplifier) and not the detector as most instrument detectors are cooled to a constant temperature. Most FPXRF instruments have a built-in automatic gain control. If the automatic gain control is allowed to make periodic adjustments, the instrument will compensate for the influence of temperature changes on its energy scale. If the FPXRF instrument has an automatic gain control function, the operator will not have to adjust the instrument's gain unless an error message appears. If an error message appears, the operator should follow the manufacturer's procedures for troubleshooting the problem. Often, this involves performing a new energy calibration. The performance of an energy calibration check to assess drift is a quality control measure discussed in Sec. 9.2.

If the operator is instructed by the manufacturer to manually conduct a gain check because of increasing or decreasing ambient temperature, it is standard to perform a gain check after every 10 to 20 sample measurements or once an hour whichever is more frequent. It is also suggested that a gain check be performed if the temperature fluctuates more than 10° F. The operator should follow the manufacturer's recommendations for gain check frequency.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The user is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

NOTE: No MSDS applies directly to the radiation-producing instrument because that is covered under the Nuclear Regulatory Commission (NRC) or applicable state regulations.

5.2 Proper training for the safe operation of the instrument and radiation training should be completed by the analyst prior to analysis. Radiation safety for each specific instrument can be found in the operator's manual. Protective shielding should never be removed by the analyst or any personnel other than the manufacturer. The analyst should be aware of the local state and national regulations that pertain to the use of radiation-producing equipment and radioactive materials with which compliance is required. There should be a person appointed within the organization that is solely responsible for properly instructing all personnel, maintaining inspection records, and monitoring x-ray equipment at regular intervals.

Licenses for radioactive materials are of two types, specifically: (1) a general license which is usually initiated by the manufacturer for receiving, acquiring, owning, possessing, using, and transferring radioactive material incorporated in a device or equipment, and (2) a specific license which is issued to named persons for the operation of radioactive instruments as required by local, state, or federal agencies. A copy of the radioactive material license (for specific licenses only) and leak tests should be present with the instrument at all times and available to local and national authorities upon request.

X-ray tubes do not require radioactive material licenses or leak tests, but do require approvals and licenses which vary from state to state. In addition, fail-safe x-ray warning lights should be illuminated whenever an x-ray tube is energized. Provisions listed above concerning radiation safety regulations, shielding, training, and responsible personnel apply to x-ray tubes just as to radioactive sources. In addition, a log of the times and operating conditions should be kept whenever an x-ray tube is energized. An additional hazard present with x-ray tubes is the danger of electric shock from the high voltage supply, however, if the tube is properly positioned within the instrument, this is only a negligible risk. Any instrument (x-ray tube or radioisotope based) is capable of delivering an electric shock from the basic circuitry when the system is inappropriately opened.

5.3 Radiation monitoring equipment should be used with the handling and operation of the instrument. The operator and the surrounding environment should be monitored continually for analyst exposure to radiation. Thermal luminescent detectors (TLD) in the form of badges and rings are used to monitor operator radiation exposure. The TLDs or badges should be worn in the area of maximum exposure. The maximum permissible whole-body dose from occupational exposure is 5 Roentgen Equivalent Man (REM) per year. Possible exposure pathways for radiation to enter the body are ingestion, inhaling, and absorption. The best precaution to prevent radiation exposure is distance and shielding.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for

use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

6.1 FPXRF spectrometer -- An FPXRF spectrometer consists of four major components: (1) a source that provides x-rays; (2) a sample presentation device; (3) a detector that converts x-ray-generated photons emitted from the sample into measurable electronic signals; and (4) a data processing unit that contains an emission or fluorescence energy analyzer, such as an MCA, that processes the signals into an x-ray energy spectrum from which elemental concentrations in the sample may be calculated, and a data display and storage system. These components and additional, optional items, are discussed below.

6.1.1 Excitation sources -- FPXRF instruments use either a sealed radioisotope source or an x-ray tube to provide the excitation source. Many FPXRF instruments use sealed radioisotope sources to produce x-rays in order to irradiate samples. The FPXRF instrument may contain between one and three radioisotope sources. Common radioisotope sources used for analysis for metals in soils are iron Fe-55 (^{55}Fe), cadmium Cd-109 (^{109}Cd), americium Am-241 (^{241}Am), and curium Cm-244 (^{244}Cm). These sources may be contained in a probe along with a window and the detector; the probe may be connected to a data reduction and handling system by means of a flexible cable. Alternatively, the sources, window, and detector may be included in the same unit as the data reduction and handling system.

The relative strength of the radioisotope sources is measured in units of millicuries (mCi). All other components of the FPXRF system being equal, the stronger the source, the greater the sensitivity and precision of a given instrument. Radioisotope sources undergo constant decay. In fact, it is this decay process that emits the primary x-rays used to excite samples for FPXRF analysis. The decay of radioisotopes is measured in "half-lives." The half-life of a radioisotope is defined as the length of time required to reduce the radioisotopes strength or activity by half. Developers of FPXRF technologies recommend source replacement at regular intervals based on the source's half-life. This is due to the ever increasing time required for the analysis rather than a decrease in instrument performance. The characteristic x-rays emitted from each of the different sources have energies capable of exciting a certain range of analytes in a sample. Table 2 summarizes the characteristics of four common radioisotope sources.

X-ray tubes have higher radiation output, no intrinsic lifetime limit, produce constant output over their lifetime, and do not have the disposal problems of radioactive sources but are just now appearing in FPXRF instruments. An electrically-excited x-ray tube operates by bombarding an anode with electrons accelerated by a high voltage. The electrons gain an energy in electron volts equal to the accelerating voltage and can excite atomic transitions in the anode, which then produces characteristic x-rays. These characteristic x-rays are emitted through a window which contains the vacuum necessary for the electron acceleration. An important difference between x-ray tubes and radioactive sources is that the electrons which bombard the anode also produce a continuum of x-rays across a broad range of energies in addition to the characteristic x-rays. This continuum is weak compared to the characteristic x-rays but can provide substantial excitation since it covers a broad energy range. It has the undesired property of producing background in the spectrum near the analyte x-ray lines when it is scattered by the sample. For this reason a filter is often used between the x-ray tube and the sample to suppress the continuum radiation while passing the characteristic x-rays from the anode. This filter is sometimes incorporated into the window of the x-ray tube. The choice of

accelerating voltage is governed both by the anode material, since the electrons must have sufficient energy to excite the anode, which requires a voltage greater than the absorption edge of the anode material and by the instrument's ability to cool the x-ray tube. The anode is most efficiently excited by voltages 2 to 2.5 times the edge energy (most x-rays per unit power to the tube), although voltages as low as 1.5 times the absorption edge energy will work. The characteristic x-rays emitted by the anode are capable of exciting a range of elements in the sample just as with a radioactive source. Table 3 gives the recommended operating voltages and the sample elements excited for some common anodes.

6.1.2 Sample presentation device -- FPXRF instruments can be operated in two modes: in situ and intrusive. If operated in the in situ mode, the probe window is placed in direct contact with the soil surface to be analyzed. When an FPXRF instrument is operated in the intrusive mode, a soil or sediment sample must be collected, prepared, and placed in a sample cup. For FPXRF instruments operated in the intrusive mode, the probe may be rotated so that the window faces either upward or downward. A protective sample cover is placed over the window, and the sample cup is placed on top of the window inside the protective sample cover for analysis.

6.1.3 Detectors -- The detectors in the FPXRF instruments can be either solid-state detectors or gas-filled, proportional counter detectors. Common solid-state detectors include mercuric iodide (HgI_2), silicon pin diode and lithium-drifted silicon Si(Li). The HgI_2 detector is operated at a moderately subambient temperature controlled by a low power thermoelectric cooler. The silicon pin diode detector also is cooled via the thermoelectric Peltier effect. The Si(Li) detector must be cooled to at least -90 °C either with liquid nitrogen or by thermoelectric cooling via the Peltier effect. Instruments with a Si(Li) detector have an internal liquid nitrogen dewar with a capacity of 0.5 to 1.0 L. Proportional counter detectors are rugged and lightweight, which are important features of a field portable detector. However, the resolution of a proportional counter detector is not as good as that of a solid-state detector. The energy resolution of a detector for characteristic x-rays is usually expressed in terms of full width at half-maximum (FWHM) height of the manganese K_α peak at 5.89 keV. The typical resolutions of the above mentioned detectors are as follows: HgI_2-270 eV; silicon pin diode-250 eV; Si(Li)–170 eV; and gas-filled, proportional counter-750 eV.

During operation of a solid-state detector, an x-ray photon strikes a biased, solid-state crystal and loses energy in the crystal by producing electron-hole pairs. The electric charge produced is collected and provides a current pulse that is directly proportional to the energy of the x-ray photon absorbed by the crystal of the detector. A gas-filled, proportional counter detector is an ionization chamber filled with a mixture of noble and other gases. An x-ray photon entering the chamber ionizes the gas atoms. The electric charge produced is collected and provides an electric signal that is directly proportional to the energy of the x-ray photon absorbed by the gas in the detector.

6.1.4 Data processing units – The key component in the data processing unit of an FPXRF instrument is the MCA. The MCA receives pulses from the detector and sorts them by their amplitudes (energy level). The MCA counts pulses per second to determine the height of the peak in a spectrum, which is indicative of the target analyte's concentration. The spectrum of element peaks are built on the MCA. The MCAs in FPXRF instruments have from 256 to 2,048 channels. The concentrations of target analytes are usually shown in ppm on a liquid crystal display (LCD) in the instrument. FPXRF instruments can store both spectra and from 3,000 to 5,000 sets of numerical analytical results. Most FPXRF instruments are menu-driven from software built into the

units or from PCs. Once the data–storage memory of an FPXRF unit is full or at any other time, data can be downloaded by means of an RS-232 port and cable to a PC.

6.2 Spare battery and battery charger.

6.3 Polyethylene sample cups – 31 to 40 mm in diameter with collar, or equivalent (appropriate for FPXRF instrument).

6.4 X-ray window film – Mylar™, Kapton™, Spectrolene™, polypropylene, or equivalent; 2.5 to 6.0 µm thick.

6.5 Mortar and pestle – Glass, agate, or aluminum oxide; for grinding soil and sediment samples.

6.6 Containers -- Glass or plastic to store samples.

6.7 Sieves – 60-mesh (0.25 mm), stainless-steel, Nylon, or equivalent for preparing soil and sediment samples.

6.8 Trowels -- For smoothing soil surfaces and collecting soil samples.

6.9 Plastic bags – Used for collection and homogenization of soil samples.

6.10 Drying oven -- Standard convection or toaster oven, for soil and sediment samples that require drying.

7.0 REAGENTS AND STANDARDS

7.1 Reagent grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Pure element standards – Each pure, single-element standard is intended to produce strong characteristic x-ray peaks of the element of interest only. Other elements present must not contribute to the fluorescence spectrum. A set of pure element standards for commonly sought analytes is supplied by the instrument manufacturer, if designated for the instrument; not all instruments require the pure element standards. The standards are used to set the region of interest (ROI) for each element. They also can be used as energy calibration and resolution check samples.

7.3 Site-specific calibration standards – Instruments that employ fundamental parameters (FP) or similar mathematical models in minimizing matrix effects may not require SSCS. If the FP calibration model is to be optimized or if empirical calibration is necessary, then SSCSs must be collected, prepared, and analyzed.

7.3.1 The SSCS must be representative of the matrix to be analyzed by FPXRF. These samples must be well homogenized. A minimum of 10 samples spanning the concentration ranges of the analytes of interest and of the interfering elements must be obtained from the site. A sample size of 4 to 8 ounces is recommended, and standard glass sampling jars should be used.

7.3.2 Each sample should be oven-dried for 2 to 4 hr at a temperature of less than 150 °C. If mercury is to be analyzed, a separate sample portion should be dried at ambient temperature as heating may volatilize the mercury. When the sample is dry, all large, organic debris and nonrepresentative material, such as twigs, leaves, roots, insects, asphalt, and rock should be removed. The sample should be homogenized (see Sec. 7.3.3) and then a representative portion ground with a mortar and pestle or other mechanical means, prior to passing through a 60-mesh sieve. Only the coarse rock fraction should remain on the screen.

7.3.3 The sample should be homogenized by using a riffle splitter or by placing 150 to 200 g of the dried, sieved sample on a piece of kraft or butcher paper about 1.5 by 1.5 feet in size. Each corner of the paper should be lifted alternately, rolling the soil over on itself and toward the opposite corner. The soil should be rolled on itself 20 times. Approximately 5 g of the sample should then be removed and placed in a sample cup for FPXRF analysis. The rest of the prepared sample should be sent off site for ICP or AA analysis. The method use for confirmatory analysis should meet the data quality objectives of the project.

7.4 Blank samples -- The blank samples should be from a "clean" quartz or silicon dioxide matrix that is free of any analytes at concentrations above the established lower limit of detection. These samples are used to monitor for cross-contamination and laboratory-induced contaminants or interferences.

7.5 Standard reference materials – Standard reference materials (SRMs) are standards containing certified amounts of metals in soil or sediment. These standards are used for accuracy and performance checks of FPXRF analyses. SRMs can be obtained from the National Institute of Standards and Technology (NIST), the U.S. Geological Survey (USGS), the Canadian National Research Council, and the national bureau of standards in foreign nations. Pertinent NIST SRMs for FPXRF analysis include 2704, Buffalo River Sediment; 2709, San Joaquin Soil; and 2710 and 2711, Montana Soil. These SRMs contain soil or sediment from actual sites that has been analyzed using independent inorganic analytical methods by many different laboratories. When these SRMs are unavailable, alternate standards may be used (e.g., NIST 2702).

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

Sample handling and preservation procedures used in FPXRF analyses should follow the guidelines in Chapter Three, "Inorganic Analytes."

9.0 QUALITY CONTROL

9.1 Follow the manufacturer's instructions for the quality control procedures specific to use of the testing product. Refer to Chapter One for additional guidance on quality assurance (QA) and quality control (QC) protocols. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results.

9.2 Energy calibration check – To determine whether an FPXRF instrument is operating within resolution and stability tolerances, an energy calibration check should be run. The energy calibration check determines whether the characteristic x-ray lines are shifting,

which would indicate drift within the instrument. As discussed in Sec. 4.10, this check also serves as a gain check in the event that ambient temperatures are fluctuating greatly (more than 10 °F).

9.2.1 The energy calibration check should be run at a frequency consistent with manufacturer's recommendations. Generally, this would be at the beginning of each working day, after the batteries are changed or the instrument is shut off, at the end of each working day, and at any other time when the instrument operator believes that drift is occurring during analysis. A pure element such as iron, manganese, copper, or lead is often used for the energy calibration check. A manufacturer-recommended count time per source should be used for the check.

9.2.2 The instrument manufacturer's manual specifies the channel or kiloelectron volt level at which a pure element peak should appear and the expected intensity of the peak. The intensity and channel number of the pure element as measured using the source should be checked and compared to the manufacturer's recommendation. If the energy calibration check does not meet the manufacturer's criteria, then the pure element sample should be repositioned and reanalyzed. If the criteria are still not met, then an energy calibration should be performed as described in the manufacturer's manual. With some FPXRF instruments, once a spectrum is acquired from the energy calibration check, the peak can be optimized and realigned to the manufacturer's specifications using their software.

9.3 Blank samples – Two types of blank samples should be analyzed for FPXRF analysis, specifically, instrument blanks and method blanks.

9.3.1 An instrument blank is used to verify that no contamination exists in the spectrometer or on the probe window. The instrument blank can be silicon dioxide, a polytetraflurorethylene (PTFE) block, a quartz block, "clean" sand, or lithium carbonate. This instrument blank should be analyzed on each working day before and after analyses are conducted and once per every twenty samples. An instrument blank should also be analyzed whenever contamination is suspected by the analyst. The frequency of analysis will vary with the data quality objectives of the project. A manufacturer-recommended count time per source should be used for the blank analysis. No element concentrations above the established lower limit of detection should be found in the instrument blank. If concentrations exceed these limits, then the probe window and the check sample should be checked for contamination. If contamination is not a problem, then the instrument must be "zeroed" by following the manufacturer's instructions.

9.3.2 A method blank is used to monitor for laboratory-induced contaminants or interferences. The method blank can be "clean" silica sand or lithium carbonate that undergoes the same preparation procedure as the samples. A method blank must be analyzed at least daily. The frequency of analysis will depend on the data quality objectives of the project. If the method blank does not contain the target analyte at a level that interferes with the project-specific data quality objectives then the method blank would be considered acceptable. In the absence of project-specific data quality objectives, if the blank is less than the lowest level of detection or less than 10% of the lowest sample concentration for the analyte, whichever is greater, then the method blank would be considered acceptable. If the method blank cannot be considered acceptable, the cause of the problem must be identified, and all samples analyzed with the method blank must be reanalyzed.

9.4 Calibration verification checks -- A calibration verification check sample is used to check the accuracy of the instrument and to assess the stability and consistency of the analysis for the analytes of interest. A check sample should be analyzed at the beginning of each working day, during active sample analyses, and at the end of each working day. The frequency of calibration checks during active analysis will depend on the data quality objectives of the project. The check sample should be a well characterized soil sample from the site that is representative of site samples in terms of particle size and degree of homogeneity and that contains contaminants at concentrations near the action levels. If a site-specific sample is not available, then an NIST or other SRM that contains the analytes of interest can be used to verify the accuracy of the instrument. The measured value for each target analyte should be within ±20 percent (%D) of the true value for the calibration verification check to be acceptable. If a measured value falls outside this range, then the check sample should be reanalyzed. If the value continues to fall outside the acceptance range, the instrument should be recalibrated, and the batch of samples analyzed before the unacceptable calibration verification check must be reanalyzed.

9.5 Precision measurements -- The precision of the method is monitored by analyzing a sample with low, moderate, or high concentrations of target analytes. The frequency of precision measurements will depend on the data quality objectives for the data. A minimum of one precision sample should be run per day. Each precision sample should be analyzed 7 times in replicate. It is recommended that precision measurements be obtained for samples with varying concentration ranges to assess the effect of concentration on method precision. Determining method precision for analytes at concentrations near the site action levels can be extremely important if the FPXRF results are to be used in an enforcement action; therefore, selection of at least one sample with target analyte concentrations at or near the site action levels or levels of concern is recommended. A precision sample is analyzed by the instrument for the same field analysis time as used for other project samples. The relative standard deviation (RSD) of the sample mean is used to assess method precision. For FPXRF data to be considered adequately precise, the RSD should not be greater than 20 percent with the exception of chromium. RSD values for chromium should not be greater than 30 percent. If both in situ and intrusive analytical techniques are used during the course of one day, it is recommended that separate precision calculations be performed for each analysis type.

The equation for calculating RSD is as follows:

$$RSD = (SD/Mean\ Concentration) \times 100$$

where:

RSD	=	Relative standard deviation for the precision measurement for the analyte
SD	=	Standard deviation of the concentration for the analyte
Mean concentration	=	Mean concentration for the analyte

The precision or reproducibility of a measurement will improve with increasing count time, however, increasing the count time by a factor of 4 will provide only 2 times better precision, so there is a point of diminishing return. Increasing the count time also improves the sensitivity, but decreases sample throughput.

9.6 The lower limits of detection should be established from actual measured performance based on spike recoveries in the matrix of concern or from acceptable method performance on a certified reference material of the appropriate matrix and within the appropriate calibration range for the application. This is considered the best estimate of the true method sensitivity as opposed to a statistical determination based on the standard deviation of

replicate analyses of a low-concentration sample. While the statistical approach demonstrates the potential data variability for a given sample matrix at one point in time, it does not represent what can be detected or most importantly the lowest concentration that can be calibrated. For this reason the sensitivity should be established as the lowest point of detection based on acceptable target analyte recovery in the desired sample matrix.

9.7 Confirmatory samples -- The comparability of the FPXRF analysis is determined by submitting FPXRF-analyzed samples for analysis at a laboratory. The method of confirmatory analysis must meet the project and XRF measurement data quality objectives. The confirmatory samples must be splits of the well homogenized sample material. In some cases the prepared sample cups can be submitted. A minimum of 1 sample for each 20 FPXRF-analyzed samples should be submitted for confirmatory analysis. This frequency will depend on project-specific data quality objectives. The confirmatory analyses can also be used to verify the quality of the FPXRF data. The confirmatory samples should be selected from the lower, middle, and upper range of concentrations measured by the FPXRF. They should also include samples with analyte concentrations at or near the site action levels. The results of the confirmatory analysis and FPXRF analyses should be evaluated with a least squares linear regression analysis. If the measured concentrations span more than one order of magnitude, the data should be log-transformed to standardize variance which is proportional to the magnitude of measurement. The correlation coefficient (r) for the results should be 0.7 or greater for the FPXRF data to be considered screening level data. If the r is 0.9 or greater and inferential statistics indicate the FPXRF data and the confirmatory data are statistically equivalent at a 99 percent confidence level, the data could potentially meet definitive level data criteria.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Instrument calibration -- Instrument calibration procedures vary among FPXRF instruments. Users of this method should follow the calibration procedures outlined in the operator's manual for each specific FPXRF instrument. Generally, however, three types of calibration procedures exist for FPXRF instruments, namely: FP calibration, empirical calibration, and the Compton peak ratio or normalization method. These three types of calibration are discussed below.

10.2 Fundamental parameters calibration -- FP calibration procedures are extremely variable. An FP calibration provides the analyst with a "standardless" calibration. The advantages of FP calibrations over empirical calibrations include the following:

- No previously collected site-specific samples are necessary, although site-specific samples with confirmed and validated analytical results for all elements present could be used.
- Cost is reduced because fewer confirmatory laboratory results or calibration standards are necessary.

However, the analyst should be aware of the limitations imposed on FP calibration by particle size and matrix effects. These limitations can be minimized by adhering to the preparation procedure described in Sec. 7.3. The two FP calibration processes discussed below are based on an effective energy FP routine and a back scatter with FP (BFP) routine. Each FPXRF FP calibration process is based on a different iterative algorithmic method. The calibration procedure for each routine is explained in detail in the manufacturer's user manual for each FPXRF instrument; in addition, training courses are offered for each instrument.

10.2.1 Effective energy FP calibration -- The effective energy FP calibration is performed by the manufacturer before an instrument is sent to the analyst. Although SSCS can be used, the calibration relies on pure element standards or SRMs such as those obtained from NIST for the FP calibration. The effective energy routine relies on the spectrometer response to pure elements and FP iterative algorithms to compensate for various matrix effects.

Alpha coefficients are calculated using a variation of the Sherman equation, which calculates theoretical intensities from the measurement of pure element samples. These coefficients indicate the quantitative effect of each matrix element on an analyte's measured x-ray intensity. Next, the Lachance Traill algorithm is solved as a set of simultaneous equations based on the theoretical intensities. The alpha coefficients are then downloaded into the specific instrument.

The working effective energy FP calibration curve must be verified before sample analysis begins on each working day, after every 20 samples are analyzed, and at the end of sampling. This verification is performed by analyzing either an NIST SRM or an SSCS that is representative of the site-specific samples. This SRM or SSCS serves as a calibration check. A manufacturer-recommended count time per source should be used for the calibration check. The analyst must then adjust the y-intercept and slope of the calibration curve to best fit the known concentrations of target analytes in the SRM or SSCS.

A percent difference (%D) is then calculated for each target analyte. The %D should be within ±20 percent of the certified value for each analyte. If the %D falls outside this acceptance range, then the calibration curve should be adjusted by varying the slope of the line or the y-intercept value for the analyte. The SRM or SSCS is reanalyzed until the %D falls within ±20 percent. The group of 20 samples analyzed before an out-of-control calibration check should be reanalyzed.

The equation to calibrate %D is as follows:

$$\%D = ((C_s - C_k) / C_k) \times 100$$

where:

%D = Percent difference
C_k = Certified concentration of standard sample
C_s = Measured concentration of standard sample

10.2.2 BFP calibration -- BFP calibration relies on the ability of the liquid nitrogen-cooled, Si(Li) solid-state detector to separate the coherent (Compton) and incoherent (Rayleigh) backscatter peaks of primary radiation. These peak intensities are known to be a function of sample composition, and the ratio of the Compton to Rayleigh peak is a function of the mass absorption of the sample. The calibration procedure is explained in detail in the instrument manufacturer's manual. Following is a general description of the BFP calibration procedure.

The concentrations of all detected and quantified elements are entered into the computer software system. Certified element results for an NIST SRM or confirmed and validated results for an SSCS can be used. In addition, the concentrations of oxygen and silicon must be entered; these two concentrations are not found in standard metals analyses. The manufacturer provides silicon and oxygen concentrations for typical soil types. Pure element standards are then analyzed using a manufacturer-recommended

count time per source. The results are used to calculate correction factors in order to adjust for spectrum overlap of elements.

The working BFP calibration curve must be verified before sample analysis begins on each working day, after every 20 samples are analyzed, and at the end of the analysis. This verification is performed by analyzing either an NIST SRM or an SSCS that is representative of the site-specific samples. This SRM or SSCS serves as a calibration check. The standard sample is analyzed using a manufacturer-recommended count time per source to check the calibration curve. The analyst must then adjust the y-intercept and slope of the calibration curve to best fit the known concentrations of target analytes in the SRM or SSCS.

A %D is then calculated for each target analyte. The %D should fall within ±20 percent of the certified value for each analyte. If the %D falls outside this acceptance range, then the calibration curve should be adjusted by varying the slope of the line the y-intercept value for the analyte. The standard sample is reanalyzed until the %D falls within ±20 percent. The group of 20 samples analyzed before an out-of-control calibration check should be reanalyzed.

10.3 Empirical calibration -- An empirical calibration can be performed with SSCS, site-typical standards, or standards prepared from metal oxides. A discussion of SSCS is included in Sec. 7.3; if no previously characterized samples exist for a specific site, site-typical standards can be used. Site-typical standards may be selected from commercially available characterized soils or from SSCS prepared for another site. The site-typical standards should closely approximate the site's soil matrix with respect to particle size distribution, mineralogy, and contaminant analytes. If neither SSCS nor site-typical standards are available, it is possible to make gravimetric standards by adding metal oxides to a "clean" sand or silicon dioxide matrix that simulates soil. Metal oxides can be purchased from various chemical vendors. If standards are made on site, a balance capable of weighing items to at least two decimal places is necessary. Concentrated ICP or AA standard solutions can also be used to make standards. These solutions are available in concentrations of 10,000 parts per million, thus only small volumes have to be added to the soil.

An empirical calibration using SSCS involves analysis of SSCS by the FPXRF instrument and by a conventional analytical method such as ICP or AA. A total acid digestion procedure should be used by the laboratory for sample preparation. Generally, a minimum of 10 and a maximum of 30 well characterized SSCS, site-typical standards, or prepared metal oxide standards are necessary to perform an adequate empirical calibration. The exact number of standards depends on the number of analytes of interest and interfering elements. Theoretically, an empirical calibration with SSCS should provide the most accurate data for a site because the calibration compensates for site-specific matrix effects.

The first step in an empirical calibration is to analyze the pure element standards for the elements of interest. This enables the instrument to set channel limits for each element for spectral deconvolution. Next the SSCS, site-typical standards, or prepared metal oxide standards are analyzed using a count time of 200 seconds per source or a count time recommended by the manufacturer. This will produce a spectrum and net intensity of each analyte in each standard. The analyte concentrations for each standard are then entered into the instrument software; these concentrations are those obtained from the laboratory, the certified results, or the gravimetrically determined concentrations of the prepared standards. This gives the instrument analyte values to regress against corresponding intensities during the modeling stage. The regression equation correlates the concentrations of an analyte with its net intensity.

The calibration equation is developed using a least squares fit regression analysis. After the regression terms to be used in the equation are defined, a mathematical equation can be developed to calculate the analyte concentration in an unknown sample. In some FPXRF instruments, the software of the instrument calculates the regression equation. The software uses calculated intercept and slope values to form a multiterm equation. In conjunction with the software in the instrument, the operator can adjust the multiterm equation to minimize interelement interferences and optimize the intensity calibration curve.

It is possible to define up to six linear or nonlinear terms in the regression equation. Terms can be added and deleted to optimize the equation. The goal is to produce an equation with the smallest regression error and the highest correlation coefficient. These values are automatically computed by the software as the regression terms are added, deleted, or modified. It is also possible to delete data points from the regression line if these points are significant outliers or if they are heavily weighing the data. Once the regression equation has been selected for an analyte, the equation can be entered into the software for quantitation of analytes in subsequent samples. For an empirical calibration to be acceptable, the regression equation for a specific analyte should have a correlation coefficient of 0.98 or greater or meet the DQOs of the project.

In an empirical calibration, one must apply the DQOs of the project and ascertain critical or action levels for the analytes of interest. It is within these concentration ranges or around these action levels that the FPXRF instrument should be calibrated most accurately. It may not be possible to develop a good regression equation over several orders of analyte concentration.

10.4 Compton normalization method – The Compton normalization method is based on analysis of a single, certified standard and normalization for the Compton peak. The Compton peak is produced from incoherent backscattering of x-ray radiation from the excitation source and is present in the spectrum of every sample. The Compton peak intensity changes with differing matrices. Generally, matrices dominated by lighter elements produce a larger Compton peak, and those dominated by heavier elements produce a smaller Compton peak. Normalizing to the Compton peak can reduce problems with varying matrix effects among samples. Compton normalization is similar to the use of internal standards in organics analysis. The Compton normalization method may not be effective when analyte concentrations exceed a few percent.

The certified standard used for this type of calibration could be an NIST SRM such as 2710 or 2711. The SRM must be a matrix similar to the samples and must contain the analytes of interests at concentrations near those expected in the samples. First, a response factor has to be determined for each analyte. This factor is calculated by dividing the net peak intensity by the analyte concentration. The net peak intensity is gross intensity corrected for baseline reading. Concentrations of analytes in samples are then determined by multiplying the baseline corrected analyte signal intensity by the normalization factor and by the response factor. The normalization factor is the quotient of the baseline corrected Compton K_{α} peak intensity of the SRM divided by that of the samples. Depending on the FPXRF instrument used, these calculations may be done manually or by the instrument software.

11.0 PROCEDURE

11.1 Operation of the various FPXRF instruments will vary according to the manufacturers' protocols. Before operating any FPXRF instrument, one should consult the manufacturer's manual. Most manufacturers recommend that their instruments be allowed to warm up for 15 to 30 minutes before analysis of samples. This will help alleviate drift or energy calibration problems later during analysis.

11.2 Each FPXRF instrument should be operated according to the manufacturer's recommendations. There are two modes in which FPXRF instruments can be operated: in situ and intrusive. The in situ mode involves analysis of an undisturbed soil sediment or sample. Intrusive analysis involves collection and preparation of a soil or sediment sample before analysis. Some FPXRF instruments can operate in both modes of analysis, while others are designed to operate in only one mode. The two modes of analysis are discussed below.

11.3 For in situ analysis, remove any large or nonrepresentative debris from the soil surface before analysis. This debris includes rocks, pebbles, leaves, vegetation, roots, and concrete. Also, the soil surface must be as smooth as possible so that the probe window will have good contact with the surface. This may require some leveling of the surface with a stainless-steel trowel. During the study conducted to provide example performance data for this method, this modest amount of sample preparation was found to take less than 5 min per sample location. The last requirement is that the soil or sediment not be saturated with water. Manufacturers state that their FPXRF instruments will perform adequately for soils with moisture contents of 5 to 20 percent but will not perform well for saturated soils, especially if ponded water exists on the surface. Another recommended technique for in situ analysis is to tamp the soil to increase soil density and compactness for better repeatability and representativeness. This condition is especially important for heavy element analysis, such as barium. Source count times for in situ analysis usually range from 30 to 120 seconds, but source count times will vary among instruments and depending on the desired method sensitivity. Due to the heterogeneous nature of the soil sample, in situ analysis can provide only "screening" type data.

11.4 For intrusive analysis of surface or sediment, it is recommended that a sample be collected from a 4- by 4-inch square that is 1 inch deep. This will produce a soil sample of approximately 375 g or 250 cm^3, which is enough soil to fill an 8-ounce jar. However, the exact dimensions and sample depth should take into consideration the heterogeneous deposition of contaminants and will ultimately depend on the desired project-specific data quality objectives. The sample should be homogenized, dried, and ground before analysis. The sample can be homogenized before or after drying. The homogenization technique to be used after drying is discussed in Sec. 4.2. If the sample is homogenized before drying, it should be thoroughly mixed in a beaker or similar container, or if the sample is moist and has a high clay content, it can be kneaded in a plastic bag. One way to monitor homogenization when the sample is kneaded in a plastic bag is to add sodium fluorescein dye to the sample. After the moist sample has been homogenized, it is examined under an ultraviolet light to assess the distribution of sodium fluorescein throughout the sample. If the fluorescent dye is evenly distributed in the sample, homogenization is considered complete; if the dye is not evenly distributed, mixing should continue until the sample has been thoroughly homogenized. During the study conducted to provide data for this method, the time necessary for homogenization procedure using the fluorescein dye ranged from 3 to 5 min per sample. As demonstrated in Secs. 13.5 and 13.7, homogenization has the greatest impact on the reduction of sampling variability. It produces little or no contamination. Often, the direct analysis through the plastic bag is possible without the more labor intensive steps of drying, grinding, and sieving given in Secs. 11.5 and 11.6. Of course, to achieve the best data quality possible all four steps should be followed.

11.5 Once the soil or sediment sample has been homogenized, it should be dried. This can be accomplished with a toaster oven or convection oven. A small aliquot of the sample (20 to 50 g) is placed in a suitable container for drying. The sample should be dried for 2 to 4 hr in the convection or toaster oven at a temperature not greater than 150 °C. Samples may also be air dried under ambient temperature conditions using a 10- to 20-g portion. Regardless of what drying mechanism is used, the drying process is considered complete when a constant sample weight can be obtained. Care should be taken to avoid sample cross-contamination and these measures can be evaluated by including an appropriate method blank sample along with any sample preparation process.

CAUTION: Microwave drying is not a recommended procedure. Field studies have shown that microwave drying can increase variability between the FPXRF data and confirmatory analysis. High levels of metals in a sample can cause arcing in the microwave oven, and sometimes slag forms in the sample. Microwave oven drying can also melt plastic containers used to hold the sample.

11.6 The homogenized dried sample material should be ground with a mortar and pestle and passed through a 60-mesh sieve to achieve a uniform particle size. Sample grinding should continue until at least 90 percent of the original sample passes through the sieve. The grinding step normally takes an average of 10 min per sample. An aliquot of the sieved sample should then be placed in a 31.0-mm polyethylene sample cup (or equivalent) for analysis. The sample cup should be one-half to three-quarters full at a minimum. The sample cup should be covered with a 2.5 µm Mylar (or equivalent) film for analysis. The rest of the soil sample should be placed in a jar, labeled, and archived for possible confirmation analysis. All equipment including the mortar, pestle, and sieves must be thoroughly cleaned so that any cross-contamination is below the established lower limit of detection of the procedure or DQOs of the analysis. If all recommended sample preparation steps are followed, there is a high probability the desired laboratory data quality may be obtained.

12.0 DATA ANALYSIS AND CALCULATIONS

Most FPXRF instruments have software capable of storing all analytical results and spectra. The results are displayed in ppm and can be downloaded to a personal computer, which can be used to provide a hard copy printout. Individual measurements that are smaller than three times their associated SD should not be used for quantitation. See the manufacturer's instructions regarding data analysis and calculations.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 The sections to follow discuss three performance evaluation factors; namely, precision, accuracy, and comparability. The example data presented in Tables 4 through 8 were generated from results obtained from six FPXRF instruments (see Sec. 13.3). The soil samples analyzed by the six FPXRF instruments were collected from two sites in the United States. The soil samples contained several of the target analytes at concentrations ranging from "nondetect" to tens of thousands of mg/kg. These data are provided for guidance purposes only.

13.3 The six FPXRF instruments included the TN 9000 and TN Lead Analyzer manufactured by TN Spectrace; the X-MET 920 with a SiLi detector and X-MET 920 with a gas-filled proportional detector manufactured by Metorex, Inc.; the XL Spectrum Analyzer manufactured by Niton; and the MAP Spectrum Analyzer manufactured by Scitec. The TN 9000 and TN Lead Analyzer both have a HgI_2 detector. The TN 9000 utilized an Fe-55, Cd-109, and Am-241 source. The TN Lead Analyzer had only a Cd-109 source. The X-Met 920 with the SiLi detector had a Cd-109 and Am-241 source. The X-MET 920 with the gas-filled proportional detector had only a Cd-109 source. The XL Spectrum Analyzer utilized a silicon pin-diode

detector and a Cd-109 source. The MAP Spectrum Analyzer utilized a solid-state silicon detector and a Cd-109 source.

13.4 All example data presented in Tables 4 through 8 were generated using the following calibrations and source count times. The TN 9000 and TN Lead Analyzer were calibrated using fundamental parameters using NIST SRM 2710 as a calibration check sample. The TN 9000 was operated using 100, 60, and 60 second count times for the Cd-109, Fe-55, and Am-241 sources, respectively. The TN Lead analyzer was operated using a 60 second count time for the Cd-109 source. The X-MET 920 with the Si(Li) detector was calibrated using fundamental parameters and one well characterized site-specific soil standard as a calibration check. It used 140 and 100 second count times for the Cd-109 and Am-241 sources, respectively. The X-MET 920 with the gas-filled proportional detector was calibrated empirically using between 10 and 20 well characterized site-specific soil standards. It used 120 second times for the Cd-109 source. The XL Spectrum Analyzer utilized NIST SRM 2710 for calibration and the Compton peak normalization procedure for quantitation based on 60 second count times for the Cd-109 source. The MAP Spectrum Analyzer was internally calibrated by the manufacturer. The calibration was checked using a well-characterized site-specific soil standard. It used 240 second times for the Cd-109 source.

13.5 Precision measurements -- The example precision data are presented in Table 4. These data are provided for guidance purposes only. Each of the six FPXRF instruments performed 10 replicate measurements on 12 soil samples that had analyte concentrations ranging from "nondetects" to thousands of mg/kg. Each of the 12 soil samples underwent 4 different preparation techniques from in situ (no preparation) to dried and ground in a sample cup. Therefore, there were 48 precision data points for five of the instruments and 24 precision points for the MAP Spectrum Analyzer. The replicate measurements were taken using the source count times discussed at the beginning of this section.

For each detectable analyte in each precision sample a mean concentration, standard deviation, and RSD was calculated for each analyte. The data presented in Table 4 is an average RSD for the precision samples that had analyte concentrations at 5 to 10 times the lower limit of detection for that analyte for each instrument. Some analytes such as mercury, selenium, silver, and thorium were not detected in any of the precision samples so these analytes are not listed in Table 4. Some analytes such as cadmium, nickel, and tin were only detected at concentrations near the lower limit of detection so that an RSD value calculated at 5 to 10 times this limit was not possible.

One FPXRF instrument collected replicate measurements on an additional nine soil samples to provide a better assessment of the effect of sample preparation on precision. Table 5 shows these results. These data are provided for guidance purposes only. The additional nine soil samples were comprised of three from each texture and had analyte concentrations ranging from near the lower limit of detection for the FPXRF analyzer to thousands of mg/kg. The FPXRF analyzer only collected replicate measurements from three of the preparation methods; no measurements were collected from the in situ homogenized samples. The FPXRF analyzer conducted five replicate measurements of the in situ field samples by taking measurements at five different points within the 4-inch by 4-inch sample square. Ten replicate measurements were collected for both the intrusive undried and unground and intrusive dried and ground samples contained in cups. The cups were shaken between each replicate measurement.

Table 5 shows that the precision dramatically improved from the in situ to the intrusive measurements. In general there was a slight improvement in precision when the sample was dried and ground. Two factors caused the precision for the in situ measurements to be poorer. The major factor is soil heterogeneity. By moving the probe within the 4-inch by 4-inch square,

measurements of different soil samples were actually taking place within the square. Table 5 illustrates the dominant effect of soil heterogeneity. It overwhelmed instrument precision when the FPXRF analyzer was used in this mode. The second factor that caused the RSD values to be higher for the in situ measurements is the fact that only five instead of ten replicates were taken. A lesser number of measurements caused the standard deviation to be larger which in turn elevated the RSD values.

13.6 Accuracy measurements – Five of the FPXRF instruments (not including the MAP Spectrum Analyzer) analyzed 18 SRMs using the source count times and calibration methods given at the beginning of this section. The 18 SRMs included 9 soil SRMs, 4 stream or river sediment SRMs, 2 sludge SRMs, and 3 ash SRMs. Each of the SRMs contained known concentrations of certain target analytes. A percent recovery was calculated for each analyte in each SRM for each FPXRF instrument. Table 6 presents a summary of this data. With the exception of cadmium, chromium, and nickel, the values presented in Table 6 were generated from the 13 soil and sediment SRMs only. The 2 sludge and 3 ash SRMs were included for cadmium, chromium, and nickel because of the low or nondetectable concentrations of these three analytes in the soil and sediment SRMs.

Only 12 analytes are presented in Table 6. These are the analytes that are of environmental concern and provided a significant number of detections in the SRMs for an accuracy assessment. No data is presented for the X-MET 920 with the gas-filled proportional detector. This FPXRF instrument was calibrated empirically using site-specific soil samples. The percent recovery values from this instrument were very sporadic and the data did not lend itself to presentation in Table 6.

Table 7 provides a more detailed summary of accuracy data for one particular FPXRF instrument (TN 9000) for the 9 soil SRMs and 4 sediment SRMs. These data are provided for guidance purposes only. Table 7 shows the certified value, measured value, and percent recovery for five analytes. These analytes were chosen because they are of environmental concern and were most prevalently certified for in the SRM and detected by the FPXRF instrument. The first nine SRMs are soil and the last 4 SRMs are sediment. Percent recoveries for the four NIST SRMs were often between 90 and 110 percent for all analytes.

13.7 Comparability – Comparability refers to the confidence with which one data set can be compared to another. In this case, FPXRF data generated from a large study of six FPXRF instruments was compared to SW-846 Methods 3050 and 6010 which are the standard soil extraction for metals and analysis by inductively coupled plasma. An evaluation of comparability was conducted by using linear regression analysis. Three factors were determined using the linear regression. These factors were the y-intercept, the slope of the line, and the coefficient of determination (r^2).

As part of the comparability assessment, the effects of soil type and preparation methods were studied. Three soil types (textures) and four preparation methods were examined during the study. The preparation methods evaluated the cumulative effect of particle size, moisture, and homogenization on comparability. Due to the large volume of data produced during this study, linear regression data for six analytes from only one FPXRF instrument is presented in Table 8. Similar trends in the data were seen for all instruments. These data are provided for guidance purposes only.

Table 8 shows the regression parameters for the whole data set, broken out by soil type, and by preparation method. These data are provided for guidance purposes only. The soil types are as follows: soil 1–sand; soil 2–loam; and soil 3–silty clay. The preparation methods are as follows: preparation 1–in situ in the field; preparation 2–intrusive, sample collected and homogenized; preparation 3–intrusive, with sample in a sample cup but sample still wet and not

ground; and preparation 4–intrusive, with sample dried, ground, passed through a 40-mesh sieve, and placed in sample cup.

For arsenic, copper, lead, and zinc, the comparability to the confirmatory laboratory was excellent with r^2 values ranging from 0.80 to 0.99 for all six FPXRF instruments. The slopes of the regression lines for arsenic, copper, lead, and zinc, were generally between 0.90 and 1.00 indicating the data would need to be corrected very little or not at all to match the confirmatory laboratory data. The r^2 values and slopes of the regression lines for barium and chromium were not as good as for the other for analytes, indicating the data would have to be corrected to match the confirmatory laboratory.

Table 8 demonstrates that there was little effect of soil type on the regression parameters for any of the six analytes. The only exceptions were for barium in soil 1 and copper in soil 3. In both of these cases, however, it is actually a concentration effect and not a soil effect causing the poorer comparability. All barium and copper concentrations in soil 1 and 3, respectively, were less than 350 mg/kg.

Table 8 shows there was a preparation effect on the regression parameters for all six analytes. With the exception of chromium, the regression parameters were primarily improved going from preparation 1 to preparation 2. In this step, the sample was removed from the soil surface, all large debris was removed, and the sample was thoroughly homogenized. The additional two preparation methods did little to improve the regression parameters. This data indicates that homogenization is the most critical factor when comparing the results. It is essential that the sample sent to the confirmatory laboratory match the FPXRF sample as closely as possible.

Sec. 11.0 of this method discusses the time necessary for each of the sample preparation techniques. Based on the data quality objectives for the project, an analyst must decide if it is worth the extra time necessary to dry and grind the sample for small improvements in comparability. Homogenization requires 3 to 5 min. Drying the sample requires one to two hours. Grinding and sieving requires another 10 to 15 min per sample. Lastly, when grinding and sieving is conducted, time has to be allotted to decontaminate the mortars, pestles, and sieves. Drying and grinding the samples and decontamination procedures will often dictate that an extra person be on site so that the analyst can keep up with the sample collection crew. The cost of requiring an extra person on site to prepare samples must be balanced with the gain in data quality and sample throughput.

13.8 The following documents may provide additional guidance and insight on this method and technique:

13.8.1 A. D. Hewitt, "Screening for Metals by X-ray Fluorescence Spectrometry/Response Factor/Compton K_α Peak Normalization Analysis," American Environmental Laboratory, pp 24-32, 1994.

13.8.2 S. Piorek and J. R. Pasmore, "Standardless, In Situ Analysis of Metallic Contaminants in the Natural Environment With a PC-Based, High Resolution Portable X-Ray Analyzer," Third International Symposium on Field Screening Methods for Hazardous Waste and Toxic Chemicals, Las Vegas, Nevada, February 24-26, 1993, Vol 2, pp 1135-1151, 1993.

13.8.3 S. Shefsky, "Sample Handling Strategies for Accurate Lead-in-soil Measurements in the Field and Laboratory," *International Symposium of Field Screening Methods for Hazardous Waste and Toxic Chemicals*, Las Vegas, NV, January 29-31, 1997.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

1. Metorex, X-MET 920 User's Manual.

2. Spectrace Instruments, "Energy Dispersive X-ray Fluorescence Spectrometry: An Introduction," 1994.

3. TN Spectrace, Spectrace 9000 Field Portable/Benchtop XRF Training and Applications Manual.

4. Unpublished SITE data, received from PRC Environment Management, Inc.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The following pages contain the tables referenced by this method. A flow diagram of the procedure follows the tables.

TABLE 1

EXAMPLE INTERFERENCE FREE LOWER LIMITS OF DETECTION

Analyte	Chemical Abstract Series Number	Lower Limit of Detection in Quartz Sand (milligrams per kilogram)
Antimony (Sb)	7440-36-0	40
Arsenic (As)	7440-38-0	40
Barium (Ba)	7440-39-3	20
Cadmium (Cd)	7440-43-9	100
Calcium (Ca)	7440-70-2	70
Chromium (Cr)	7440-47-3	150
Cobalt (Co)	7440-48-4	60
Copper (Cu)	7440-50-8	50
Iron (Fe)	7439-89-6	60
Lead (Pb)	7439-92-1	20
Manganese (Mn)	7439-96-5	70
Mercury (Hg)	7439-97-6	30
Molybdenum (Mo)	7439-93-7	10
Nickel (Ni)	7440-02-0	50
Potassium (K)	7440-09-7	200
Rubidium (Rb)	7440-17-7	10
Selenium (Se)	7782-49-2	40
Silver (Ag)	7440-22-4	70
Strontium (Sr)	7440-24-6	10
Thallium (Tl)	7440-28-0	20
Thorium (Th)	7440-29-1	10
Tin (Sn)	7440-31-5	60
Titanium (Ti)	7440-32-6	50
Vanadium (V)	7440-62-2	50
Zinc (Zn)	7440-66-6	50
Zirconium (Zr)	7440-67-7	10

Source: Refs. 1, 2, and 3
These data are provided for guidance purposes only.

TABLE 2

SUMMARY OF RADIOISOTOPE SOURCE CHARACTERISTICS

Source	Activity (mCi)	Half-Life (Years)	Excitation Energy (keV)	Elemental Analysis Range	
Fe-55	20-50	2.7	5.9	Sulfur to Chromium Molybdenum to Barium	K Lines L Lines
Cd-109	5-30	1.3	22.1 and 87.9	Calcium to Rhodium Tantalum to Lead Barium to Uranium	K Lines K Lines L Lines
Am-241	5-30	432	26.4 and 59.6	Copper to Thulium Tungsten to Uranium	K Lines L Lines
Cm-244	60-100	17.8	14.2	Titanium to Selenium Lanthanum to Lead	K Lines L Lines

Source: Refs. 1, 2, and 3

TABLE 3

SUMMARY OF X-RAY TUBE SOURCE CHARACTERISTICS

Anode Material	Recommended Voltage Range (kV)	K-alpha Emission (keV)	Elemental Analysis Range	
Cu	18-22	8.04	Potassium to Cobalt Silver to Gadolinium	K Lines L Lines
Mo	40-50	17.4	Cobalt to Yttrium Europium to Radon	K Lines L Lines
Ag	50-65	22.1	Zinc to Technicium Ytterbium to Neptunium	K Lines L Lines

Source: Ref. 4

Notes: The sample elements excited are chosen by taking as the lower limit the same ratio of excitation line energy to element absorption edge as in Table 2 (approximately 0.45) and the requirement that the excitation line energy be above the element absorption edge as the upper limit (L2 edges used for L lines). K-beta excitation lines were ignored.

TABLE 4

EXAMPLE PRECISION VALUES

Analyte	Average Relative Standard Deviation for Each Instrument at 5 to 10 Times the Lower Limit of Detection					
	TN 9000	TN Lead Analyzer	X-MET 920 (SiLi Detector)	X-MET 920 (Gas-Filled Detector)	XL Spectrum Analyzer	MAP Spectrum Analyzer
Antimony	6.54	NR	NR	NR	NR	NR
Arsenic	5.33	4.11	3.23	1.91	12.47	6.68
Barium	4.02	NR	3.31	5.91	NR	NR
Cadmium	29.84[a]	NR	24.80[a]	NR	NR	NR
Calcium	2.16	NR	NR	NR	NR	NR
Chromium	22.25	25.78	22.72	3.91	30.25	NR
Cobalt	33.90	NR	NR	NR	NR	NR
Copper	7.03	9.11	8.49	9.12	12.77	14.86
Iron	1.78	1.67	1.55	NR	2.30	NR
Lead	6.45	5.93	5.05	7.56	6.97	12.16
Manganese	27.04	24.75	NR	NR	NR	NR
Molybdenum	6.95	NR	NR	NR	12.60	NR
Nickel	30.85[a]	NR	24.92[a]	20.92[a]	NA	NR
Potassium	3.90	NR	NR	NR	NR	NR
Rubidium	13.06	NR	NR	NR	32.69[a]	NR
Strontium	4.28	NR	NR	NR	8.86	NR
Tin	24.32[a]	NR	NR	NR	NR	NR
Titanium	4.87	NR	NR	NR	NR	NR
Zinc	7.27	7.48	4.26	2.28	10.95	0.83
Zirconium	3.58	NR	NR	NR	6.49	NR

These data are provided for guidance purposes only.
Source: Ref. 4

[a] These values are biased high because the concentration of these analytes in the soil samples was near the lower limit of detection for that particular FPXRF instrument.

NR Not reported.

NA Not applicable; analyte was reported but was below the established lower limit detection.

TABLE 5

EXAMPLES OF PRECISION AS AFFECTED BY SAMPLE PREPARATION

Analyte	Average Relative Standard Deviation for Each Preparation Method		
	In Situ-Field	Intrusive-Undried and Unground	Intrusive-Dried and Ground
Antimony	30.1	15.0	14.4
Arsenic	22.5	5.36	3.76
Barium	17.3	3.38	2.90
Cadmium[a]	41.2	30.8	28.3
Calcium	17.5	1.68	1.24
Chromium	17.6	28.5	21.9
Cobalt	28.4	31.1	28.4
Copper	26.4	10.2	7.90
Iron	10.3	1.67	1.57
Lead	25.1	8.55	6.03
Manganese	40.5	12.3	13.0
Mercury	ND	ND	ND
Molybdenum	21.6	20.1	19.2
Nickel[a]	29.8	20.4	18.2
Potassium	18.6	3.04	2.57
Rubidium	29.8	16.2	18.9
Selenium	ND	20.2	19.5
Silver[a]	31.9	31.0	29.2
Strontium	15.2	3.38	3.98
Thallium	39.0	16.0	19.5
Thorium	NR	NR	NR
Tin	ND	14.1	15.3
Titanium	13.3	4.15	3.74
Vanadium	NR	NR	NR
Zinc	26.6	13.3	11.1
Zirconium	20.2	5.63	5.18

These data are provided for guidance purposes only.
Source: Ref. 4
[a] These values may be biased high because the concentration of these analytes in the soil samples was near the lower limit of detection.
ND Not detected.
NR Not reported.

TABLE 6

EXAMPLE ACCURACY VALUES

Analyte	Instrument															
	TN 9000				TN Lead Analyzer				X-MET 920 (SiLi Detector)				XL Spectrum Analyzer			
	n	Range of % Rec.	Mean % Rec.	SD	n	Range of % Rec.	Mean % Rec.	SD	n	Range of % Rec.	Mean % Rec	SD	n	Range of % Rec.	Mean % Rec.	SD
Sb	2	100-149	124.3	NA	--	--	--	--	--	--	--	--	--	--	--	--
As	5	68-115	92.8	17.3	5	44-105	83.4	23.2	4	9.7-91	47.7	39.7	5	38-535	189.8	206
Ba	9	98-198	135.3	36.9	--	--	--	--	9	18-848	168.2	262	--	--	--	--
Cd	2	99-129	114.3	NA	--	--	--	--	6	81-202	110.5	45.7	--	--	--	--
Cr	2	99-178	138.4	NA	--	--	--	--	7	22-273	143.1	93.8	3	98-625	279.2	300
Cu	8	61-140	95.0	28.8	6	38-107	79.1	27.0	11	10-210	111.8	72.1	8	95-480	203.0	147
Fe	6	78-155	103.7	26.1	6	89-159	102.3	28.6	6	48-94	80.4	16.2	6	26-187	108.6	52.9
Pb	11	66-138	98.9	19.2	11	68-131	97.4	18.4	12	23-94	72.7	20.9	13	80-234	107.3	39.9
Mn	4	81-104	93.1	9.70	3	92-152	113.1	33.8	--	--	--	--	--	--	--	--
Ni	3	99-122	109.8	12.0	--	--	--	--	--	--	--	--	3	57-123	87.5	33.5
Sr	8	110-178	132.6	23.8	--	--	--	--	--	--	--	--	7	86-209	125.1	39.5
Zn	11	41-130	94.3	24.0	10	81-133	100.0	19.7	12	46-181	106.6	34.7	11	31-199	94.6	42.5

Source: Ref. 4. These data are provided for guidance purposes only.
n: Number of samples that contained a certified value for the analyte and produced a detectable concentration from the FPXRF instrument.
SD: Standard deviation; NA: Not applicable; only two data points, therefore, a SD was not calculated.
%Rec.: Percent recovery.
-- No data.

TABLE 7

EXAMPLE ACCURACY FOR TN 9000[a]

Standard Reference Material	Arsenic			Barium			Copper			Lead			Zinc		
	Cert. Conc.	Meas. Conc.	%Rec.	Cert. Conc.	Meas. Conc.	%Rec.	Cert. Conc.	Meas. Conc.	%Rec.	Cert. Conc.	Meas. Conc.	%Rec.	Cert. Conc.	Meas. Conc.	%Rec.
RTC CRM-021	24.8	ND	NA	586	1135	193.5	4792	2908	60.7	144742	149947	103.6	546	224	40.9
RTC CRM-020	397	429	92.5	22.3	ND	NA	753	583	77.4	5195	3444	66.3	3022	3916	129.6
BCR CRM 143R	--	--	--	--	--	--	131	105	80.5	180	206	114.8	1055	1043	99.0
BCR CRM 141	--	--	--	--	--	--	32.6	ND	NA	29.4	ND	NA	81.3	ND	NA
USGS GXR-2	25.0	ND	NA	2240	2946	131.5	76.0	106	140.2	690	742	107.6	530	596	112.4
USGS GXR-6	330	294	88.9	1300	2581	198.5	66.0	ND	NA	101	80.9	80.1	118	ND	NA
NIST 2711	105	104	99.3	726	801	110.3	114	ND	NA	1162	1172	100.9	350	333	94.9
NIST 2710	626	722	115.4	707	782	110.6	2950	2834	96.1	5532	5420	98.0	6952	6476	93.2
NIST 2709	17.7	ND	NA	968	950	98.1	34.6	ND	NA	18.9	ND	NA	106	98.5	93.0
NIST 2704	23.4	ND	NA	414	443	107.0	98.6	105	106.2	161	167	103.5	438	427	97.4
CNRC PACS-1	211	143	67.7	--	772	NA	452	302	66.9	404	332	82.3	824	611	74.2
SARM-51	--	--	--	335	466	139.1	268	373	139.2	5200	7199	138.4	2200	2676	121.6
SARM-52	--	--	--	410	527	128.5	219	193	88.1	1200	1107	92.2	264	215	81.4

Source: Ref. 4. These data are provided for guidance purposes only.

[a] All concentrations in milligrams per kilogram.

%Rec.: Percent recovery; ND: Not detected; NA: Not applicable.

-- No data.

TABLE 8

EXAMPLE REGRESSION PARAMETERS FOR COMPARABILITY[1]

	Arsenic				Barium				Copper			
	n	r^2	Int.	Slope	n	r^2	Int.	Slope	n	r^2	Int.	Slope
All Data	824	0.94	1.62	0.94	1255	0.71	60.3	0.54	984	0.93	2.19	0.93
Soil 1	368	0.96	1.41	0.95	393	0.05	42.6	0.11	385	0.94	1.26	0.99
Soil 2	453	0.94	1.51	0.96	462	0.56	30.2	0.66	463	0.92	2.09	0.95
Soil 3	—	—	—	—	400	0.85	44.7	0.59	136	0.46	16.60	0.57
Prep 1	207	0.87	2.69	0.85	312	0.64	53.7	0.55	256	0.87	3.89	0.87
Prep 2	208	0.97	1.38	0.95	315	0.67	64.6	0.52	246	0.96	2.04	0.93
Prep 3	204	0.96	1.20	0.99	315	0.78	64.6	0.53	236	0.97	1.45	0.99
Prep 4	205	0.96	1.45	0.98	313	0.81	58.9	0.55	246	0.96	1.99	0.96

	Lead				Zinc				Chromium			
	n	r^2	Int.	Slope	n	r^2	Int.	Slope	n	r^2	Int.	Slope
All Data	1205	0.92	1.66	0.95	1103	0.89	1.86	0.95	280	0.70	64.6	0.42
Soil 1	357	0.94	1.41	0.96	329	0.93	1.78	0.93	—	—	—	—
Soil 2	451	0.93	1.62	0.97	423	0.85	2.57	0.90	—	—	—	—
Soil 3	397	0.90	2.40	0.90	351	0.90	1.70	0.98	186	0.66	38.9	0.50
Prep 1	305	0.80	2.88	0.86	286	0.79	3.16	0.87	105	0.80	66.1	0.43
Prep 2	298	0.97	1.41	0.96	272	0.95	1.86	0.93	77	0.51	81.3	0.36
Prep 3	302	0.98	1.26	0.99	274	0.93	1.32	1.00	49	0.73	53.7	0.45
Prep 4	300	0.96	1.38	1.00	271	0.94	1.41	1.01	49	0.75	31.6	0.56

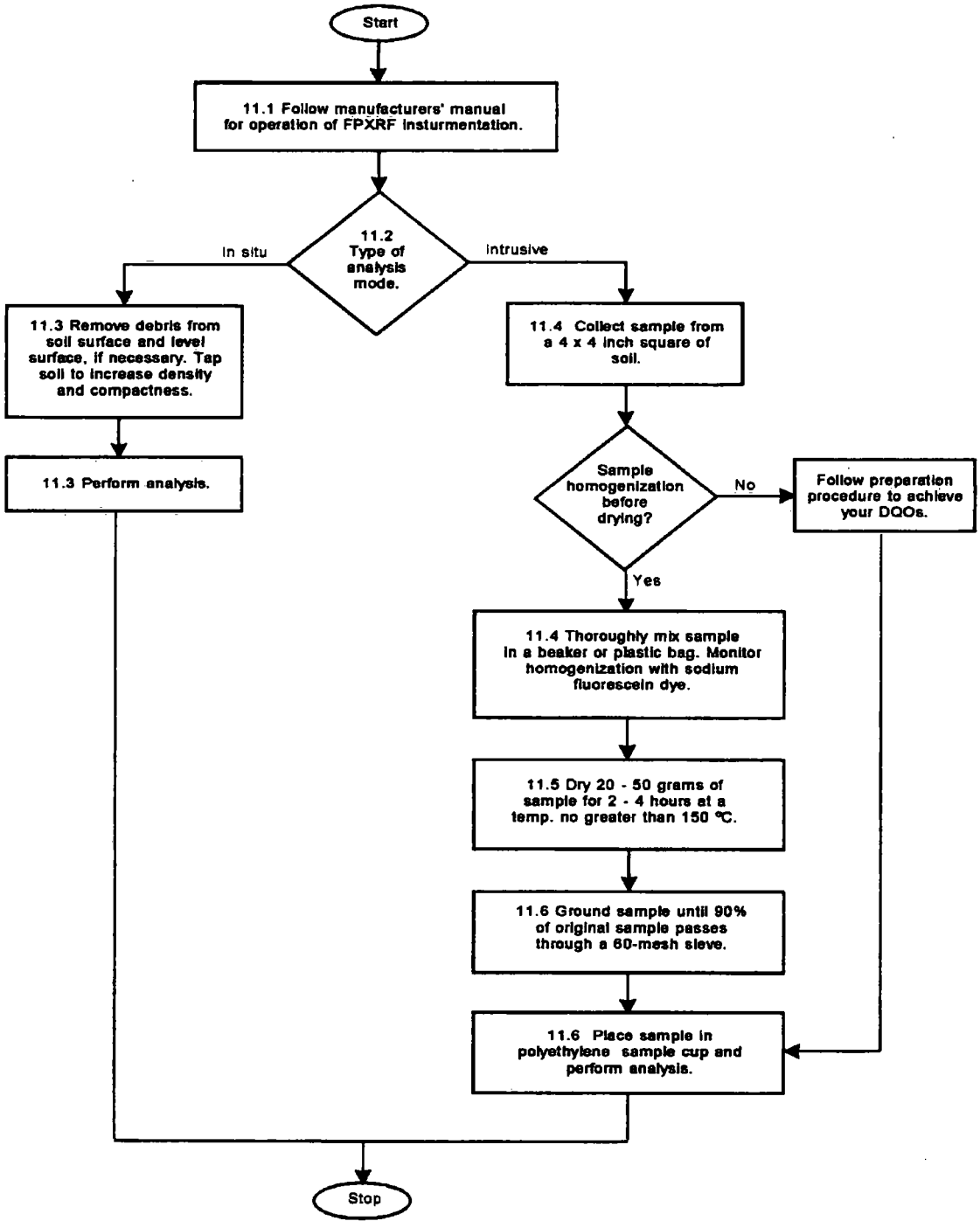
Source: Ref. 4. These data are provided for guidance purposes only.

[1] Log-transformed data

n: Number of data points; r^2: Coefficient of determination; Int.: Y-intercept

— No applicable data

FIELD PORTABLE X-RAY FLUORESCENCE SPECTROMETRY FOR THE DETERMINATION OF ELEMENTAL CONCENTRATIONS IN SOIL AND SEDIMENT



Attachment 2

Niton FXL User's Guide (Electronic Copy on CD)

Appendix C

Sample Handling, Packing, and Shipping Standard Operating Procedures

Appendix C: Sample Handling, Packing, and Shipping Standard Operating Procedures

Sample Handling

After collecting a sample, the following procedures are followed:

- Record the following information on the daily field log sheets or in the field notebook, as appropriate:
  - Project name and number;
  - Sample number and depth;
  - Sampling method;
  - Date;
  - Name of sampler(s);
  - Sample collection time (military);
  - Location (project reference);
  - Analyses to be completed;
  - Sample medium (e.g., soil, water); and
  - Any comments.
- Fill in sample label with:
  - Project number;
  - Sample number;
  - Sample interval (if applicable);
  - Sample type (composite or grab);
  - Sample matrix (soil);
  - Date;
  - Sample collection time (military);
  - Analyses required;
  - Initials of the sampling personnel; and
  - Preservative added, if applicable.
- Ensure that all sample labels are securely affixed to the sample container with clear packing tape.
- Check the caps on the sample containers to ensure that they are tightly sealed.

- Complete the chain-of-custody (COC) form with the required sampling information and ensure that the recorded information matches the sample labels. Initial the COC form after sample packing. **NOTE:** If the designated sampling person relinquishes the samples to other sampling or field personnel for packing or other purposes, the samplers will complete the COC prior to this transfer. The appropriate personnel will sign and date the COC form to document the sampling custody transfer.

Sample Splitting

The soil samples that are collected as part of the off-site soils pilot study will be analyzed for metals using both XRF analysis and laboratory analysis. Samples will also be analyzed for pH and soil moisture. The following procedures describe how the samples will be handled for both analyses.

1. Upon receipt of the sample in the field laboratory, the XRF technician will check the COC forms with the sample labels to assure that all the samples are present and correctly labeled.
2. Prior to performing the XRF analysis, the XRF technician will remove an aliquot of soil for XRF analysis (consistent with Appendix B – Procedures for Metals Analysis Using Field Portable X-Ray Fluorescence Analyzers). The lid will be replaced on the remaining sample for possible laboratory analysis.
3. For those samples that are shipped to the laboratory for analysis, the COC procedures outlined in Step 1 above will be followed.

Packing

The following procedures will be used when shipping samples to the analytical laboratory:

- Using packing or duct tape, secure the outside and inside of the drain plug at the bottom of the cooler that is used for sample transport.
- Wrap bottles in bubble wrap or other cushioning material.
- Place 1 or 2 inches of cushioning material at the bottom of the cooler.
- Place the sealed sample containers in the cooler.
- Repackage ice in sealed plastic bags and place loosely in the cooler.
- Fill the remaining space in the cooler with cushioning material.
- Place COC form(s) in a sealed plastic bag, and tape the forms to the inside of the cooler lid.
- Close the lid of the cooler and fasten with packing tape.
- Wrap strapping tape around both end of the cooler at least twice.
- Mark the cooler on the outside with the following information: shipping address, return address, "Fragile" labels, and arrows indicating "This Side Up". Cover the labels with clear plastic tape. Place signed custody seal label over cooler lid.

Shipping

- All samples will be hand-delivered or delivered by an express carrier to the project laboratory.
- The following COC procedures will apply to sample shipping:
  - Relinquish the sample containers to the laboratory via express carrier. The signed and dated COC form(s) should be included in the cooler, as described above. The express carrier will not be required to sign the COC forms. The sampler should retain the express carrier receipt of bill of lading.
  - When the samples are received by the laboratory, the laboratory personnel shall complete the COC forms be recording receipt of samples, and compare the sample identification numbers on the containers with the COC forms.

Appendix D

Equipment Cleaning and Decontamination Standard Operating Procedures

Appendix D: Equipment Cleaning and Decontamination Standard Operating Procedures

Introduction

The equipment cleaning procedures described herein include pre-field, in the field, and post-field cleaning of sampling equipment. The sampling equipment consists of soil sampling equipment and other activity-specific sampling equipment. The non-disposable equipment will be cleaned after completing each sampling event.

Materials

The following materials will be available for cleaning equipment:

- Health and safety equipment;
- Distilled water;
- Non-phosphate soap (Alconox or equivalent);
- Tap water;
- Rinse collection plastic containers;
- Brushes;
- Plastic sheeting;
- Large heavy duty, clear plastic bags;
- Alconox/water mix applicable bottles;
- Ziploc® type bags;
- Handiwipes; and
- Field notebook,

Storage of Equipment

All sampling equipment will be stored in a clean environment and, where appropriate, the equipment will be contained in clear plastic bags if the equipment will be stored overnight or will not be used immediately.

Health and Safety Precautions

Personnel will wear health and safety equipment (e.g., safety glasses), as specified in the Health and Safety Plan (HASP).

Field Cleaning Procedures

Small field equipment cleaning areas will be selected as locations away from the immediate work area and upwind so as not to adversely impact the cleaning procedure, but close enough to the sampling personnel and a water source to keep equipment handling to a minimum.

The field sampling equipment cleaning procedures are as follows:

- Select equipment cleaning location;
- Wash/Scrub with non-phosphate detergent and tap water;
- Rinse with tap water;
- Rinse with deionized or distilled water;
- Air dry or blot off with clean white paper towels; and
- Contain in plastic garbage bags, if necessary.

Waste Disposal Methods

Consistent with the existing Site-wide FSP (Golder, 1999a) and Addendum (ENVIRON, 2006), decontamination rinsate may be discharged directly to ground surface on the former plant site area. Decontamination rinsate will not be discharged to the ground surface on the residential properties.

APPENDIX D

Appendix D

QAPP Addendum

Quality Assurance Project Plan Addendum OU4: Off-Site Soils

DePue Site
DePue, Illinois

Prepared for:
Illinois Environmental Protection Agency

Prepared by:
ENVIRON International Corporation
Chicago, Illinois

Date:
October 2013

Project Number:
21-12406C

ENVIRON

Contents

1 Introduction

This Quality Assurance Project Plan Addendum (QAPP Addendum) has been prepared to cover the soil analysis included in the Off-Site Soils Design Study (the "Design Study") and the Off-Site Soils Pilot Study (the "Pilot Study") for OU4. These studies will be collectively referred to as "OU4 Studies" in the following sections of this document. This QAPP Addendum supplements the existing Phase II Remedial Investigation QAPP Addendum (ENVIRON, 2007), and the *Quality Assurance Project Plan Addendum for the Removal Action Limit Assessment* (RAL QAPP) (Blasland, Bouck & Lee, Inc. [BBL], 2005). The RAL QAPP is included in Appendix A.

Additional details concerning specific aspects of the work described in this QAPP Addendum are provided in supporting documents such as the RAL Field Sampling Plan (FSP) Addendum (ENVIRON, 2013), and site-wide Health and Safety Plan (HASP) Addendum (ENVIRON, 2006). Certain activities, which are not addressed in the previous versions of these documents, require an addendum.

The following sections outline the amendments to the RAL QAPP. Those sections of the RAL QAPP that do not apply to the OU4 Studies, or that do not require amending, are not included in this QAPP Addendum.

2 QAPP Amendments

QAPP deletions, corrections, and amendments are provided in the appropriate sections below.

Section 2.1.1 Overall Project Management

The table in Section 2.1.1 for overall project management applicable to the Design Study and Pilot Study is as follows:

Company/Organization	Title	Name	Phone Number
IEPA	Project Manager	Charlene Falco	217-785-2891
DePue Group	Co-Project Coordinators	Mark Travers Joseph Abel	312-288-3890 401-434-7356
ENVIRON	Principal-In Charge	Mark Travers	312-288-3890
	Project Manager	Ryan Keeler	312-288-3833
	Field Manager	TBD	TBD
	Quality Assurance Coordinator	TBD	TBD
Shealy Environmental, Inc.	Project Manager	Kelly Maberry	803-227-2706
	Quality Assurance Officer	Jami Savie	803-791-9700
ALS Global	Project Manager	TBD	360-577-7222
	Quality Assurance Officer	TBD	360-577-7222

Section 2.1.2 Task Managers

The table in Section 2.1.2 for task managers applicable to the Design Study and Pilot Study is as follows:

Company/Organization	Title	Name	Phone Number
ENVIRON	Field Task Manager	TBD	TBD
	Survey Task Manager	TBD	TBD
	Health and Safety Officer	Mark Watka	312-288-3875
	Database Administrator	TBD	TBD
Laboratory Data Consultants, Inc.	Data Validator	Linda Routo	760-634-0437 Ext 138

Section 3 Objectives for Measurement Data

Step 1: Problem Statement

The list of Human Health constituents of potential concern (HCOPC) for the Pilot Study and Design Study are summarized in Table 1. The ecological constituents of potential concern (ECOPC) analyte list and other analysis proposed for ecological habitat areas are also summarized in Table 1. Laboratory analysis for inorganic analytes will be completed using Contract Laboratory Program (CLP) Method ISM 01.3 or most recent method. Laboratory analysis for hexavalent chromium will be completed using EPA Method 7196, cation exchange using SW-846 Method 9081, pH using SW-846 Method 9045C, Total Organic Carbon using ASTM Method D4129, and particle size using ASTM Method D422. Exchangeable metals analysis will be completed using a neutral salt extraction using calcium nitrate and analyzing the inorganic analytes using EPA Methods 6010/6020/7471.

Section 4.2 Sample Containers and Preservation

The sample containers and preservation methods, analytical methods, and laboratory holding times for the OU4 Studies soil samples are summarized in Table 2.

Section 4.3 Sample Chain-of-Custody

An example chain-of-custody form is included in Appendix B.

Section 4.6 Sample Codes

All soil samples will be assigned a unique sample name and sample identification number. The sample name will be used on sample labels, chain of custody sheets, and field logbooks. The soil samples will be identified similar to the designation outlined in BBL Field Change Request No. 1. The sample name for discrete soil samples will begin with "OU4" for Operable Unit 4, followed by "SS" for soil sample, followed by a sequential property number starting at 18 (Property designations 1 through 17 were used during the RAL), followed by the soil boring number for the property (e.g., 04), followed by the sample depth in inches (e.g., 0-1). An example sample name for a discrete soil sample obtained from 0 to 1 inch below ground surface (bgs) from soil boring 3 at OU4 property 22 is: OU4-SS-22-03(0-1). For composite samples, the soil boring identification will be replaced with the composite area identifier for the composite area (i.e., COMP 2). An example sample name for a composite sample obtained from composite area 2 on the above property is: OU4-SS-22-COMP2(0-1). Quality Assurance/Quality Control samples will be identified as outlined in the RAL QAPP Addendum (BBL, 2005).

The sample identification number will be an eight-digit number. The first four digits will identify the year, and the next four numbers will be a unique sequential identifier for each sample. An example sample identification number for a sample collected in 2013 is 20130035.

Section 7 Analytical Procedures

The analytical procedures to be used by the fixed based laboratory for the Pilot Study and the Design Study are summarized in Table 1. Field analyses using XRF will be completed using EPA Method 6200.

3 References

Arcadis. 2011. Final Background Soil Sampling Report. New Jersey Zinc/Mobil Chemical Site, Chicago, Illinois.

Blasland, Bouck & Lee (BBL). 2005a. Removal Action Limit Assessment Work Plan. DePue Site. Syracuse, NY.

ENVIRON International Corporation (ENVIRON). 2007. Quality Assurance Project Plan Addendum, Phase II On-Site Remedial Investigation, DePue Site, DePue, Illinois. February.

ENVIRON. 2011. Removal Action Limit Assessment Report. Prepared for the DePue Group by ENVIRON International Corporation, Chicago, Illinois.

ENVIRON. 2012. Off-Site Soils Design Study. Prepared for the DePue Group by ENVIRON International Corporation, Chicago, Illinois.

United States Environmental Protection Agency (USEPA). 1989. Statistical Methods for Evaluating the Attainment of Cleanup Standards, EPA 230/02-89-042, Washington, DC.

USEPA. 2003. Superfund Lead-Contaminated Residential Sites Handbook. OSWER 9285.7-50.

USEPA. 2009. Statistical Analysis of Groundwater Monitoring Data at RCRA Facilities, EPA 530/R-09-007, Washington, DC.

USEPA. 2010. ProUCL Version 4.1.00. Technical Guide (Draft). Statistical Software for Environmental Applications for Data Sets with and without Nondetect Observations, EPA 600/R-07/041, Washington, DC

Tables

TABLE 1

Analyte List
OU4 Off-Site Soils
DePue Site
DePue, Illinois

CLP Inorganics	CLP ICP-AES CRQL, Waters, mg/L	CLP ICP-AES CRQL, Soils, mg/kg	Precision/RPD (waters/soils)	Accuracy/Recovery (all media)
Human Health Constituents of Potential Concern (HCOPC)				
Antimony	0.06	6	≤20%/≤35%	LCS 70% - 130% (Except Antimony 50% - 150%) MS 75% - 125%
Arsenic	0.01	1		
Barium	0.2	20		
Cadmium	0.005	0.5		
Chromium	0.01	1		
Cobalt	0.05	5		
Copper	0.025	2.5		
Iron	0.1	10		
Lead	0.01	1		
Manganese	0.015	1.5		
Thallium	0.025	2.5		
Zinc	0.06	6		
Mercury	0.0002	0.1	≤20%	75% - 125%
Ecological Constituents of Potential Concern (ECOPC)				
Aluminum	0.2	20	≤20%/≤35%	LCS 70% - 130% (Except Antimony 50% - 150%) MS 75% - 125%
Antimony	0.06	6		
Arsenic	0.01	1		
Barium	0.2	20		
Beryllium	0.005	0.5		
Cadmium	0.005	0.5		
Chromium	0.01	1		
Cobalt	0.05	5		
Copper	0.025	2.5		
Iron	0.1	10		
Lead	0.01	1		
Manganese	0.015	1.5		
Nickel	0.04	4		
Selenium	0.035	3.5		
Silver	0.01	1		
Thallium	0.025	2.5		
Vanadium	0.05	5		
Zinc	0.06	6		
Cyanide	0.01	0.5		
Mercury	0.0002	0.1	≤20%	75% - 125%
Other				
Hexavalent Chromium (EPA 7196)	0.02	1	20% RPD	90% - 110%
pH (9045C)	NA	±0.1 units	≤35%RPD	NA
Cation Exchange Capacity (EPA 9081)	NA	NA	≤20%/≤35%	75% - 125%
Total Organic Carbon (ASTM D4129)	10	50	≤20%/≤35%	75% - 125%
Exchangeable Metals[1]	NA	NA	NA	NA
Particle size (ASTM D422*)	NA	NA	NA	NA

Notes:

CLP: Contract Laboratory Program
ICP-AES: Inductively Coupled Plasma-Atomic Emission Spectroscopy
CRQL: Contract Required Quantitation Limit (ISM01.3)
HCOPC: Human Health Constituent of Potential Concern
ECOPC: Ecological Constituent of Potential Concern
LCS: Laboratory Control Sample
MS: Matrix Spike

[1] Neutral Salt Extraction using Calcium Nitrate, inorganics analysis using EPA Methods 6010/6020

TABLE 2

Sample Containers, Preservatives, and Holding Times
OU4 Off-Site Soils
DePue Site
DePue, Illinois

Analytical Category	Laboratory	Matirx	Container Type	Preservation	Maximum Holding Time
CLP Inorganics	Shealy	Soil	4-oz. glass jar with teflon-lined lid, XRF sample cup, or plastic baggie	Cool 4°C±2°	Analyze in 6 months
pH (9045C)	Shealy	Soil	4-oz. glass jar with teflon-lined lid	Cool 4°C±2°	Analyze in 6 months
Hexavalent Chromium (EPA 7196)	Shealy	Soil	4-oz. glass jar with teflon-lined lid	Cool 4°C±2°	Analyze in 28 days
Cation Exchange Capacity (EPA 9081)	ALS Global	Soil	4-oz. glass jar with teflon-lined lid	Cool 4°C±2°	Analyze in 6 months
Total Organic Carbon (ASTM D4129)	ALS Global	Soil	4-oz. glass jar with teflon-lined lid	Cool 4°C±2°	Analyze in 6 months
Exchangeable Metals[1]	ALS Global	Soil	4-oz. glass jar with teflon-lined lid	Cool 4°C±2°	Analyze in 6 months
Particle size (ASTM D422*)	ALS Global	Soil	8-oz glass jar	None	None

Notes:

[1] Neutral Salt Extraction using Calcium Nitrate, inorganics analysis using EPA Methods 6010/6020/7471

Appendix A

RAL QAPP

Quality Assurance Project Plan Addendum Removal Action Limit Assessment DePue Site

The DePue Group
DePue, Illinois

May 2005

BBL®
BLASLAND, BOUCK & LEE, INC.
engineers, scientists, economists

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Attachments

Distribution List

Organization	Individual
DePue Group:	
Viacom International, Inc.	Jeff Groy
Environ (on behalf of Viacom International, Inc.)	Mark Travers
ExxonMobil	Joseph A. Abel
Terra Environmental, Inc. (on behalf of ExxonMobil)	Steven T. Walker
Blasland, Bouck & Lee, Inc. (BBL)	Nancy Gensky, David Hohreiter, David Rigg, Dennis Capria, Rick DiFiore, Todd Merrell
Illinois Environmental Protection Agency	Richard M. Lange
Lancaster Laboratories	Megan Moeller

DEPUE SITE – DEPUE, ILLINOIS
OFF-SITE SOILS REMEDIAL INVESTIGATION

QUALITY ASSURANCE PROJECT PLAN ADDENDUM

Prepared By: Blasland, Bouck & Lee, Inc.

Approved:

_____
Project Manager
Blasland, Bouck & Lee, Inc.

Approved:

_____
Quality Assurance Coordinator
Blasland, Bouck & Lee, Inc.

Approved:

_____
Project Manager
(Lancaster Laboratories)

Approved:

_____
Quality Assurance Manager
(Lancaster Laboratories)

Approved:

_____
Project Manager
(Illinois Environmental Protection Agency)

Acronyms

BBL	Blasland, Bouck & Lee, Inc.
BT	Biota Sample
CLP	Contract Laboratory Program
COC	Chain of Custody
COPC	Chemical of Potential Concern
CSP	Certified Safety Professional
CSV	Comma-Separated Value
DQO	Data Quality Objective
EDD	Electronic Data Deliverable
ERA	Ecological Risk Assessment
FSP	Field Sampling Plan
GIS	Geographic Information System
HHRA	Human Health Risk Assessment
IDEH	Illinois Department of Public Health
IEPA	Illinois Environmental Protection Agency
MS	Matrix Spike
MSD	Matrix Spike Duplicate
NCP	National Contingency Plan
OSWER	Office of Solid Waste and Emergency Response
OU	Operable Unit
PRPs	Potentially Responsible Parties
QAC	Quality Assurance Coordinator
QAPP	Quality Assurance Project Plan
QA/QC	Quality Assurance/Quality Control
RAL	Removal Action Limit
RI/FS	Remedial Investigation/Feasibility Study
SOP	Standard Operating Procedure
SS	Soil Sample
USEPA	U.S. Environmental Protection Agency

1. Project Objectives and Specific Tasks

The objectives and specific field and laboratory investigation steps are described in the *Removal Action Limit Assessment Work Plan (BBL, 2005a)* for the initial sampling and analysis at residential properties and the field reconnaissance. Likewise, the objectives and specific field and laboratory investigation steps for any additional sampling and analysis at residential properties will follow the same objectives and steps as the initial sampling. Similarly, the objectives and specific field and laboratory investigation steps for the off-site soils RI will be set forth in the *Off-Site Soils Remedial Investigation Work Plan* (to be developed).

Specific sampling protocols [including standard operating procedures (SOPs)] are provided in the Field Sampling Plan Addendum (BBL, 2005b).

2. Project Organization and Responsibilities

2.1 Project Organization

Investigations performed as part of the RAL Assessment and Offsite Soil RI will require integration of personnel from the organizations identified below, including the potentially responsible parties (PRPs) collectively referred to as the "DePue Group." The responsibilities of each member of the project team are described below.

2.1.1 Overall Project Management

On behalf of the DePue Group, BBL has overall responsibility for the RAL Assessment and Offsite Soil RI activities. BBL personnel will perform related sampling activities. In addition, BBL personnel will evaluate data and prepare the deliverables as specified in the Work Plans. Project direction will be provided by the DePue Group with oversight by the Illinois Environmental Protection Agency (IEPA). Key project management personnel are listed below.

Company/Organization	Title	Name	Phone Number
IEPA	Project Manager	Richard M. Lange	815-447-2125
DePue Group	Co-Project Coordinators	Mark Travers Joseph Abel	312-853-9430 x 217 401-434-7356
BBL	Project Officer	David W. Hohreiter	315-446-9120 x 402
	Project Manager	Nancy Gensky	312-332-4937 x 13
	Field Manager	Todd Merrell	315-446-9120 x 368
	Quality Assurance Coordinator	Dennis Capria	315-446-9120 x 299
Lancaster Laboratories	Project Manager	Mike Kramer	717-656-2308 x1988
	Quality Assurance Manager	Megan Moeller	717-656-2308 x1246

2.1.2 Task Managers

The BBL personnel performing the RAL Assessment and RI will be directed by representatives of the project team. The personnel responsible for each of the Site activities are listed below.

Company/Organization	Title	Name	Phone Number
BBL	Field Task Manager	TBD	TBD
	Survey Task Manager	TBD	TBD
	Risk Assessment Task Manager	David K. Rigg	(315) 446-9120 x 405
	Health and Safety Officer	Jay D. Keough, Certified Safety Professional (CSP)	(609) 860-0590 x 101
	Database Administrator	TBD	(315) 446-9120
	Data Validator	Dennis Capria	(315) 446-9120 x 299

2.2 Team Member Responsibilities

The responsibilities of the various team members are summarized below by organization.

2.2.1 DePue Group

Co-Project Coordinators

Responsibilities and duties include:

- Provide overall direction of DePue Group actions;
- Direct BBL; and
- Review BBL work products, including data, memoranda, letters, reports, and all other documents transmitted to the IEPA.

2.2.2 BBL

Project Officer

Responsibilities and duties include:

- Oversee BBL work products; and
- Provide BBL approval for major project deliverables.

Project Manager

Responsibilities and duties include:

- Manage and coordinate the project as defined in the Work Plans, with an emphasis on adhering to the project objectives;
- Review documents prepared by BBL; and
- Provide that corrective actions are taken for deficiencies cited during any audits.

Task Managers

The Work Plan components will be managed by various Task Managers, as set forth in Section 2.1.2. Responsibilities and duties of each Task Manager include, as appropriate:

- Manage relevant day-to-day activities;
- Develop, establish, and maintain files on relevant project activities;
- Review data reductions from the relevant project activities;
- Perform final data review of field data reductions and reports on relevant project activities;
- Provide that corrective actions are taken for deficiencies cited during audits of relevant project activities;
- Perform overall quality assurance/quality control (QA/QC) of the relevant portions of the project activities;

- Review relevant field records and logs;
- Instruct personnel working on relevant project activities;
- Coordinate field and laboratory schedules pertaining to relevant project activities;
- Request sample bottles from laboratory;
- Review the field instrumentation, maintenance, and calibration to meet quality objectives;
- Prepare reports pertaining to relevant project activities; and
- Maintain field and laboratory files of notebooks and logs, data reductions, and calculations, and transmit originals to the Project Manager.

Field Personnel

Responsibilities and duties include:

- Perform field procedures associated with the investigations as set forth in the Work Plans, FSP, FSP Addendum;
- Perform field analyses and collect QA samples;
- calibrate, operate, and maintain field equipment;
- Reduce field data;
- Maintain sample custody; and
- Prepare field records and logs.

Quality Assurance Coordinator (QAC)

Responsibilities and duties include:

- Review laboratory data packages;
- Oversee and interface with the analytical laboratory;
- Coordinate field QA/QC procedures with Task Managers, including audits of field activities, concentrating on field analytical measurements and practices to meet data quality objectives;
- Review field reports;
- Perform and review audit reports;
- Prepare interim QA/QC compliance reports; and
- Prepare a QA/QC report in accordance with U.S. Environmental Protection Agency (USEPA) guidelines, which includes an evaluation of field and laboratory data and data usability reports.

2.2.3 Analytical Laboratories

General responsibilities and duties of the analytical laboratories include:

- Perform sample analyses and associated laboratory QA/QC procedures;
- Supply sample containers and shipping cartons;
- Maintain laboratory custody of sample; and
- Strictly adhere to all protocols in the QAPP.

Project Manager

Responsibilities and duties include:

- Serve as primary communication link between BBL and laboratory technical staff;
- Monitor workloads and facilitate availability of resources;
- Oversee preparation of analytical reports; and
- Supervise in-house chain of custody (COC).

Quality Assurance Manager

Responsibilities and duties include:

- Supervise the group that reviews and inspects all project-related laboratory activities; and
- Conduct audits of all laboratory activities.

2.2.4 IEPA

Project Manager

Responsibilities and duties include:

- Provide IEPA review and approval of the Work Plans, supporting documents, and future deliverables; and
- Monitor progress of investigation activities.

3. Objectives for Measurement Data

The data quality objectives (DQO) process, as described in the USEPA QAPP instructions document, is intended to provide a "logical framework" for planning field investigations. This section addresses, in turn, each of the seven sequential steps in the USEPA QAPP DQO process.

Step 1: Problem Statement

Previous offsite soils investigations have indicated the presence of constituents of potential concern (COPC). These COPC have the potential to adversely affect human health and the environment. The sampling and analysis program is intended to generate data to support a RAL assessment, a baseline risk assessment, and a feasibility study (FS) of potential remedial alternatives.

Step 2: Decision Identification

The initial use of the data is descriptive for characterizing the distribution of metals in soils from offsite areas. Review of the descriptive information will include a comparison of the offsite soils data to RALs (see Table 4). The need for further investigation and/or remedial activities will be based (in part) on whether RALs are exceeded.

Data from the RAL Assessment may also be used in subsequent phases of the investigation to conduct baseline risk assessment activities, and (if necessary) to evaluate remedial alternatives and soil disposal methods.

Step 3: Identifying Decision Inputs

Decision inputs incorporate both concentration and distribution of COPC in off-site soils. A fundamental basis for decision-making is that a sufficient number of data points of acceptable quality are available from the investigation to support the decision. Thus, the necessary inputs for the decision are: 1) the proportion of non-rejected (usable) data points; 2) the proportion of acceptable correlation of data collected by USEPA SW-846 method 6200 (XRF screening method) and USEPA SW-846 method 6000/7000 (laboratory confirmatory data which at a minimum will be approximately twenty percent (20%) of data analyzed by the method 6200); and 3) the quantity of data needed to evaluate whether there are unacceptable risks to human health and the environment present at the Site.

The data will be evaluated for completeness, general conformance with requirements of this QAPP Addendum, and consistency among datasets and with historical data, as appropriate.

Step 4: Defining the Study Boundaries

The boundaries for this QAPP Addendum are specific to OU4, which includes residential properties outlined in the *RAL Assessment Work Plan* and the preliminary off-site soils study area.

Step 5: Developing a Decision Rule

The decision about whether data can be used in the risk assessment will be based on: 1) the acceptable correlation between inorganic data collected by the XRF (Screening method) and laboratory (confirmatory method); and 2) the validation results. As cited in USEPA method SW-846 6200 the data correlation will be evaluated by the following procedure: *"The confirmatory samples will be selected from the lower, middle, and upper range of concentrations measured by the XRF. They should also include samples with analyte*

concentrations at or near the site action levels. The results of the confirmatory analysis and XRF analyses should be evaluated with a least squares linear regression analysis. If the measured concentrations span more than one order of magnitude, the data should be log-transformed to standardize variance which is proportional to the magnitude of measurement. The correlation coefficient (r2) for the results should be 0.7 or greater for the XRF data to be considered screening level data. If the r2 is 0.9 or greater and inferential statistics indicate the XRF data and the confirmatory data are statistically equivalent at a 99 percent confidence level, the data could potentially meet definitive level data criteria."

Following validation, the data will be flagged, as appropriate, and any use restrictions noted. The sampling plan was devised so that the loss of any single data point will not hinder description of the distribution of constituents of concern or the development of a risk assessment. Given these parameters, a reasonable decision rule would be that as long as more than 90% of data points are retained, the data may be considered usable for site characterization and risk assessment purposes.

Step 6: Limits on Decision Errors

Specifications for this step call for:

- Giving forethought to corrective actions to improve data usability; and
- Understanding the representative nature of the sampling design.

This QAPP Addendum was designed to meet both specifications for this step. Corrective actions are described elsewhere in the document. The representative nature of the sampling design was evaluated via discussions among professionals familiar with the DePue Site and the IEPA.

Step 7: Design Optimization

The overall QA objective is to develop and implement procedures for field sampling, COC, laboratory analysis, and reporting that will provide results to support the baseline risk assessments (i.e., human health and ecological), and be consistent with NCP requirements. Specific procedures for sampling, COC, laboratory instrument calibration, laboratory analysis, data reporting, internal QC, audits, preventive maintenance of field equipment, and corrective action are described in other sections of this QAPP Addendum.

The sampling plan involves a phased approach to both sampling and analysis. This provides the opportunity to evaluate and focus each data collection step to optimize the overall data collection process.

4. Sampling Procedures

4.1 General

The soil samples will be collected as part of the RAL Assessment and Off-site Soils RI. Specific sampling protocols (including SOPs) are provided in the FSP Addendum (BBL, 2005b).

Differences between the existing Site-wide QAPP and this QAPP Addendum are presented below.

4.2 Sample Containers and Preservation

Appropriate sample containers, preservation methods, analytical methods, and laboratory holding times for soil sampling activities are provided in Table 2.

The analytical laboratory will supply appropriate sample containers and preservatives, as necessary. The bottles will be purchased pre-cleaned, according to USEPA Office of Solid Waste and Emergency Response (OSWER) Directive 9240.05A requirements. Field personnel will be responsible for properly labeling containers and preserving samples (as appropriate).

4.3 Sample Chain of Custody (COC)

The objective of field sample custody is to provide that samples are not tampered with from the time of collection through time of transport to the analytical laboratory. Individuals will have "custody of samples" when the samples are in their physical possession, in their view after being in their possession, or in their physical possession and secured so they cannot be tampered with. In addition, when samples are secured in a restricted area accessible only to authorized personnel, they will be deemed to be in the custody of such authorized personnel.

Field custody documentation consists of both field logbooks and field COC forms.

4.4 Cleaning and Decontamination of Sampling Equipment

Decontamination and cleaning of sampling equipment is discussed in the FSP Addendum.

4.5 Management of Investigation-Derived Materials and Wastes

Management of investigation-derived materials and wastes is discussed in the FSP Addendum. Specifically, disposable equipment (including personal protective equipment) and debris will be containerized and appropriately labeled during the sampling events, and will be disposed by the DePue Group in accordance with applicable regulations. Consistent with the existing Site-wide FSP, decontamination rinsate may be discharged directly to ground surface, as approved previously by IEPA. However, acid wash solution will be containerized at the decontamination station, and upon completion of the field activities, the rinsate will be containerized in a

steel drum or polyethylene tank for storage in a suitable onsite location prior to treatment at the on-site wastewater treatment plant. Support facilities for material storage and staging will be properly located at the Former Plant Site Area.

4.6 Sample Codes

Samples will be identified using a unique designation system that will facilitate sample tracking. The sample designation system to be employed will be consistent from sample to sample, yet flexible enough to accommodate unforeseen sampling events and conditions. An alpha-numeric system will be used by field personnel to assign each sample a unique sample identification number. As demonstrated below, the sample identification number will begin with a three character prefix indicating the sample location by the Operable Unit (OU), followed by two letters indicating the sample type (i.e., SS for soil), two digits indicating property location, and two digits indicating the sample location. Additional information (e.g., sample depth) will be appended to the end of the sample identification.

For each property, the two digit sample number beginning with "01" for the first location will be assigned in the field and increased by one as samples are collected from additional locations.

For example, consider the following sample identification label:

OU4-SS-01-01-(0-1")

This sample is an offsite soils investigation (OU4) soil sample (SS) collected from the first property (01), is the first soil sampling location from that property (01), and is from a depth of 0 to 1 inches (0-1").

For composite samples, an additional alpha-character will be added after the sample number to indicate the subsample (i.e. "a", "b", "c", "d", and "e" for five subsamples of a five-point composite) and additional alpha-characters will be added after the depth interval to indicate a composite "COMP" sample.

For example, consider the following sample identification label:

OU4-SS-01-01a-(0-1")
OU4-SS-01-01COMP-(0-1")

The first sample is an offsite soils investigation (OU4) soil sample (SS) collected from the first property (01), collected from the first subsample location of the first soil sampling location (01a) from a depth of 0 to 1 inches (0-1") and is a discrete sample. The second sample is an offsite soils investigation (OU4) soil sample (SS), collected from the first property (01), is a composite collected at the first soil sampling location (01COMP), and is from a depth of 0 to 1 inches (0-1").

Additional sample volumes collected for matrix spike (MS) and matrix spike duplicate (MSD) analysis will be noted on the chain-of-custody (COC) forms, and the associated additional sample containers will be labeled with the appropriate suffix (i.e., MS or MSD). Rinse blanks will use the same coding scheme noted above, substituting the location code with the prefix "RB" (e.g., the first rinse blank associated with soil collection would be named OU4-RBSS-001). Field duplicates will be labeled as ordinary field samples with a unique identification number. Duplicate samples will not be identified, and the laboratory will analyze them as "blind" QC samples.

5. Sample Custody

5.1 Field Documentation and Custody Procedures

Field personnel will provide comprehensive documentation pertaining to various aspects of field sampling, field analysis, and sample COC. This documentation consists of a record that allows reconstruction of field events to aid in the data review and interpretation process. Documents, records, and information relating to the performance of the field work will be retained in the project file.

As noted in Section 4, the objective of field sample custody is to provide that samples are not tampered with from the time of sample collection through time of transport to the analytical laboratory. Individuals will have "custody of samples" when the samples are in their physical possession, in their view after being in their possession, or in their physical possession and secured so they cannot be tampered with. In addition, when samples are secured in a restricted area accessible only to authorized personnel, they will be deemed to be in the custody of such authorized personnel.

Field custody documentation consists of field logbooks, sample labels, and field COC forms.

5.1.1 Field Logbooks

Field logbooks will provide the means of recording data collecting activities performed. As such, entries will be described in as much detail as possible so that parties visiting the field locations could re-construct a particular situation without reliance on memory.

Field logbooks will be bound field survey books or notebooks. Logbooks will be assigned to field personnel, but will be stored in a secure location when not in use. Each logbook will be identified by the project-specific document number. The title page of each logbook will contain the following:

- Person to whom the logbook is assigned;
- Logbook number;
- Project name;
- Project start date; and
- End date.

Entries into the logbook will contain a variety of information. At the beginning of each entry, the date, start time, weather, names of all sampling team members present, level of personal protection being used, and signature of the person making the entry will be entered. The names of visitors to the field activity location, field sampling or investigation team personnel, and the purpose of their visit will also be recorded in the field logbook.

Measurements made and samples collected will be recorded. Entries will be made in ink, and no erasures will be made. If an incorrect entry is made, the information will be crossed out with one strike mark. Whenever a sample is collected or a measurement is made, a detailed description of the location of the station will be recorded. The number of the photographs taken of the station, if any, will also be noted. All equipment used to make measurements will be identified, along with the date of calibration.

Samples will be collected following the sampling procedures documented in the FSP Addendum. The equipment used to collect samples will be noted, along with the time of sampling, sample description, depth at which the sample was collected, volume, and number of containers used. Sample identification numbers will be assigned prior to sample collection. Field duplicate samples, which will receive an entirely separate sample identification number, will be noted under sample description.

5.1.2 Sample Labeling

Preprinted sample labels will be affixed to sample bottles prior to delivery at the sampling location. The following information is required on each sample label:

- Project;
- Date collected;
- Time collected;
- Location;
- Sampler;
- Analysis to be performed;
- Preservative; and
- Sample number.

5.1.3 Field COC Forms

Completed COC forms will be required for all samples to be analyzed. COC forms will be initiated by the sampling crew in the field. The COC forms (Attachment A) will contain the unique sample identification number, sample date and time, sample description, sample type, preservation (if any), and analyses required. The original COC form will accompany the samples to the laboratory. Copies of the COC form will be made prior to shipment (or multiple copy forms will be used) for field documentation. The COC forms will remain with the samples at all times. The samples and signed COC forms will remain in the possession of the sampling crew until the samples are delivered to the express carrier (e.g., Federal Express), hand delivered to a mobile or permanent laboratory, or placed in secure storage.

Sample labels will be completed for each sample using waterproof ink. The labels will include sample information such as: sample number and location, type of sample, date and time of sampling, sampler's name or initials, preservation, and analyses to be performed. The completed sample labels will be affixed to each sample bottle and covered with clear tape.

Whenever samples are split with a government agency or other party, a separate COC will be prepared for those samples and marked to indicate with whom the samples are being split. The person relinquishing the samples to the facility or agency should request the representative's signature acknowledging sample receipt. If the representative is unavailable or refuses, this will be noted in the "Received By" space.

5.2 Packing, Handling, and Shipping Requirements

Sample packaging and shipment procedures are designed so that the samples will arrive intact at the laboratory, along with the COC.

Samples will be packaged for shipment as outlined in Attachment B of the FSP Addendum. Specifically, the following procedures will apply:

- Securely affix the sample labels to the sample containers with clear packing tape.
- Verify that caps on the sample containers are properly sealed.
- Wrap the sample container cap with clear packing tape to prevent it from becoming loose.
- Complete the COC form with the required sampling information and match the recorded information to the sample labels. **NOTE:** If the designated sampler relinquishes the samples to other sampling or field personnel for packing or other purposes, the sampler will complete the COC prior to this transfer. The appropriate personnel will sign and date the COC form to document the sample custody transfer.
- Using duct tape, secure the outside drain plug at the bottom of the cooler.
- Wrap sample containers in bubble wrap or other cushioning material.
- Place 1 to 2 inches of cushioning material at the bottom of the cooler.
- Place the sealed sample containers into the cooler.
- Place ice in plastic bags and seal; place loosely in the cooler.
- Fill the remaining space in the cooler with cushioning material.
- Place COC forms in a plastic bag and seal; tape the forms to the inside of the cooler lid.
- Close the lid of the cooler, lock, and secure with duct tape.
- Wrap strapping tape around both ends of the cooler at least twice.
- Mark the cooler on the outside with the following information: shipping address, return address, "Fragile" labels, and arrows indicating "this side up;" cover the labels with clear plastic tape; place a signed custody seal over the sample cooler lid.

The original COC form will accompany the shipment; copies will be retained by the sampler for the sampling office records. If the samples are sent by common carrier, a bill of lading will be used. Receipts or bills of lading will be retained as part of the permanent project documentation. Commercial carriers are not required to sign off on the COC form as long as the forms are sealed inside the sample cooler and the custody seals remain intact.

Sample custody seals and packing materials for filled sample containers will be provided by the analytical laboratory. The filled, labeled, and sealed containers will be placed in a cooler on ice and carefully packed to eliminate the possibility of container breakage.

Additional procedures for packing, handling, and shipping environmental samples are presented in SOPs presented in the FSP Addendum.

6. Calibration Procedures

The field instrument calibration procedures will be consistent with the existing Site-wide QAPP with exception of the addition of the metals analysis completed by XRF methodology USEPA SW-846 6200. The calibration procedure specific to this method can be found in the FSP SOP Attachment B.

7. Analytical Procedures

The analytical procedures for this investigation are listed in Table 3-1 of the existing Site-wide QAPP with the exception of the addendum to Table 3-1 of metals analysis performed by XRF methodology USEPA SW-846 6200.

USEPA SW-846 6200 Analytes of interest, PQL, and QA/QC

Analytes	Approximate PQL	Precision RPD	Correlation of Confirmatory Sampling
arsenic (As)	13	Field sample will be analyzed seven times in replicate at a frequency of one per day or 1 per 20 samples or whichever greater. All analytes with the exception of chromium should not exhibit a relative standard deviation (RSD) of the replicates of greater than 20 percent. Chromium should not exhibit a RSD greater than 30 percent.	Acceptable correlation is discussed in Section 8.1.
barium (Ba)	100		
cadmium (Cd)	50		
chromium (Cr)	45		
cobalt (Co)	200		
copper (Cu)	50		
iron (Fe)	100		
lead (Pb)	16		
manganese (Mn)	80		
mercury (Hg)	14		
nickel (Ni)	70		
selenium (Se)	9		
silver (Ag)	45		
zinc (Zn)	30		

Notes:
These are approximate PQLs expressed in units of mg/kg. The project-specific PQLs and MDLs will be determined as described in FSP Attachment B as defined in the QA/QC section 7.0.

8. Data Reduction, Validation, and Reporting

8.1 Data Reporting

Three data categories were defined to address various analytical data uses and the associated QA/QC effort and methods required to achieve the desired levels of quality. These categories are:

- **Screening Data:** Screening data affords a quick assessment of site characteristics or conditions. This objective for data quality is applicable to data collection activities that involve rapid, non-rigorous methods of analysis and QA. This objective is generally applied to physical and/or chemical properties of samples, degree of contamination relative to concentration differences, and preliminary health and safety assessment.

- **Screening Data with Definitive Confirmation:** Screening data allows rapid identification and quantitation, although the quantitation can be relatively imprecise. This objective for data quality is available for data collection activities that require qualitative and/or quantitative verification of a select portion of sample findings (10% or more). This objective can also be used to verify less rigorous laboratory-based methods.

- **Definitive Data:** Definitive data are generated using analytical methods, such as approved USEPA reference methods. Data are analyte-specific, with confirmation of analyte identity and concentration. Methods produce raw data (e.g., chromatograms, spectra, digital values) in the form of paper printouts or computer-generated electronic files.

It is anticipated that both screening and definitive data categories will be used during the investigation. Field analysis of inorganic parameters by USEPA method SW-846 6200 which will be obtained during the off-site soil sampling for use in qualitatively interpreting data versus the RALs will be dependent on acceptable data correlation between data obtain by the use of methods 6200 and 6010B/7000. The acceptable data correlation criterion presented in the table below is provided in USEPA document *"Environmental Technology Verification Report EPA/600/R-97/150"*.

Data Correlation Between Methods SW-846 6200 and SW-846 6010B/7471A

Data Quality Level	Acceptable Data Correlation
Screening Data (Qualitative)	r2 = less than 0.70. The precision (RSD) is greater than 20 percent. The data must have less than a 10 percent false negative rate.
Screening Data with Definitive Confirmation (Quantitative)	r2 = 0.70 to 1.0. The precision (RSD) must be less than 20 percent, but the inferential statistics indicate that the data sets are statistically different.
Definitive Data	r2 = 0.85 to 1.0. The precision (RSD) must be less than or equal to 10 percent and the inferential statistics must indicate that the two data sets are statistically similar.

For this project, three levels of data reporting have been defined. They are as follows:

- **Level 1:** Minimal Reporting: Minimal or "results-only" reporting is used for analyses that, either due to their nature (i.e., field monitoring) or the intended data use (i.e., preliminary screening), do not generate or require extensive supporting documentation.

- **Level 2:** Modified Reporting: Modified reporting is used for analyses that are performed following standard USEPA-approved methods and QA/QC protocols. Based on the intended data use, modified reporting may require some supporting documentation but not, however, full Contract Laboratory Program- (CLP-) reporting.

- **Level 3:** Full Reporting: Full CLP reporting is used for those analyses that, based on the intended data use, require full documentation.

8.2 Data Management

The purpose of data management is to provide that all of the necessary data are accurate and readily accessible to meet the analytical and reporting objectives of the project. The field investigations will encompass a large number of samples and analytes from a large geographic area. Due to the large amount of resulting data, the need arises for a structured, comprehensive, and efficient program to manage the data.

The data management program established for the project includes field documentation and sample QA/QC procedures, methods for tracking and managing the data, and a system for filing all site-related information. More specifically, data management procedures will be employed to efficiently process the information collected such that the data are readily accessible and accurate. These procedures are described in detail in the following section.

The data management program has four elements:

1) Sample designation system;
2) Field activities;
3) Sample tracking and management; and
4) Data management system.

8.3 Sample Designation System

A concise and easily understandable sample designation system is an important part of the project sampling activities. It provides a unique sample number that will facilitate both sample tracking and easy re-sampling of select locations to evaluate data gaps, if necessary. The sample designation system to be employed during the sampling activities will be consistent, yet flexible enough to accommodate unforeseen sampling events or conditions. A combination of letters and numbers will be used to yield a unique sample number for each field sampled collected, as outlined in Section 4.

8.4 Field Activities

Field activities designed to gather the information necessary to make decisions during the RI process require consistent documentation and accurate record keeping. During project activities, standardized procedures will be used to document field activities, data security, and QA.

8.4.1 Field Documentation

Complete and accurate record keeping is a critical component of the field investigation activities. When interpreting analytical results and identifying data trends, field notes are an important part of the review and validation process. To thoroughly document the field investigation, several different information records, each with its own specific reporting requirements, will be maintained, including:

- Field logs;
- XRF Analytical logs; and
- COC forms.

Each of these types of field documentation is described below.

Field Logs

The personnel performing field activities will keep field logs that detail all observations and measurements made during the RAL Assessment and Off-site Soils RI. Data will be recorded directly into dedicated, bound notebooks, with each entry dated and signed. To provide at any future date that notebook pages are not missing, each page will be sequentially numbered. Erroneous entries will be corrected by crossing out the original entry, initialing it, and then documenting the proper information. In addition, certain media sampling locations will be surveyed to accurately record their locations. The survey crew will use their own field logs and will supply the sampling location coordinates to the Database Administrator.

Analytical Logs

The personnel performing XRF analysis will keep an analytical database log that will detail all observations and measurements made during the RAL Assessment and Off-site Soils RI. Data will be recorded directly into dedicated, database. An audit trail will be providing documentation of any erroneous entries corrected in the database by initialing and dating the changed data. The analytical log will include the sample identification (ID) as outlined in Section 4.5.1 and a XRF ID. This will serve as a cross reference between the field sample ID and the XRF ID. The XRF ID will include the type of sample either field sample (FS) or quality control sample (QC) followed by sequentially increasing number (e.g., QC-1, QC-2, FS-1, FS-2). This identification process will enable electronic data collected for the XRF to be cross-referenced to the original field sample ID in the database.

COC Forms

COC forms are used to document and track sample possession from time of collection to the time of disposal. A COC form will accompany each field sample collected, and one copy of the form will be filed in the field office. All field personnel will be briefed on the proper use of the COC procedure. A sample COC form is included in Attachment A of this QAPP Addendum.

8.4.2 Data Security

Measures will be taken during the field investigation so that samples and records are not lost, damaged, or altered. When not in use, all field notebooks will be stored at the field office or locked in the field vehicle. Access to these files will be limited to the field personnel who use them.

8.5 Sample Management and Tracking

A record of all field documentation will be maintained to promote the validity of data used in the Site analysis. To effectively execute such documentation, specific sample tracking and data management procedures will be used throughout the sampling program.

Sample tracking will begin with the completion of COC forms as summarized in Section 5. The completed COC forms will be faxed and/or emailed to the QAC. Copies of all completed COC forms will be maintained in the field office. The laboratory will verify receipt of the samples electronically (i.e., via email) on the following day.

When analytical data are received from the laboratory, the QAC will review the incoming analytical data packages against the information on the COCs to confirm that the correct analyses were performed for each sample and that results for all samples submitted for analysis were received. Any discrepancies noted will be promptly followed up by the QAC.

8.6 Data Management System

In addition to the sample tracking system, a data management system will be implemented. The central focus of the data management system will be developing a personal computer-based project database. The project database, to be maintained by the Database Administrator, will combine pertinent geographical, field, and analytical data. Information that will be used to populate the database will be derived from three primary sources: surveying sampling locations, field observations, and analytical results. Each of these sources is discussed in the following subsections.

8.6.1 Computer Hardware

The database will be constructed on Pentium-based personal computer work stations connected through a Novell network server. The Novell network will provide access to various hardware peripherals (e.g., laser printers, backup storage devices, image scanners, modems, etc). Computer hardware will be upgraded in the future to maintain industrial and corporate standards, as necessary.

8.6.2 Computer Software

The database will be written in Microsoft® Access, running in a Windows operating system. Custom applets, such as diskette importing programs, will be written in either Microsoft VBA or Microsoft Visual Basic. Geographic Information System (GIS) applications will be developed in ESRI ArcGIS, with additional customization performed with Visual Basic. Tables and other database reports will be generated through Access

in conjunction with Microsoft Excel, Microsoft Word, and/or Seagate Crystal Reports. These software products will be upgraded to current industrial standards, as necessary.

8.6.3 Survey Information

Sample location will be surveyed to accurately document sample locations for mapping and GIS purposes, to facilitate the re-sampling of select sample locations during future monitoring programs, if needed, and for any additional activities. Surveying activities will consist of collecting information that will be used to compute northing and easting in state plane coordinates (NAD 83, feet) for each sample location and collecting information to compute elevations relative to the for select sample locations, as appropriate. All field books associated with the surveying activities will be stored as a record of the project activities.

8.6.4 Field Observations

An important component of the information that will ultimately reside in the data management system for use during the project will originate in the observations that are recorded in the field.

During each sampling event, appropriate field documentation will be prepared by the field personnel who performed the sampling activities. The purpose of the documentation is to create a summary and record of the sampling event. Items to be included are the locations sampled, sampling methodologies used, blind duplicate and MS/MSD sample identification numbers, equipment decontamination procedures, personnel involved in the activity, and any other noteworthy events that occurred.

8.6.5 Analytical Results

Analytical results will be provided by the laboratory in both a digital and a hard copy format. The data packages will be examined to provide that the correct analyses were performed for each sample submitted and that all of the analyses requested on the COC form were performed. If discrepancies are noted, the QAC will be notified and will promptly follow up with the laboratory to resolve any issues.

Each data package will be validated in accordance with the procedures presented in the existing QAPP. Any data that does not meet the specified standards will be flagged pending resolution of the issue. The flag will not be removed from the data until the issue associated with the sample results is resolved. Although flags may remain for certain data, the use of that data may not necessarily be restricted.

Following completion of the data validation, the digital files will be used to populate the appropriate database tables. An example of the electronic data deliverable (EDD) format is included in Table 3. This format specifies one data record for each constituent and each sample analyzed. Specific fields include:

- Sample identification number;
- Date sampled;
- Date analyzed;
- Parameter name;
- Analytical result;
- Units;
- Detection limit; and

- Qualifier(s).

The individual EDDs, supplied by the laboratory in either an ASCII comma-separated value (CSV) format or in a Microsoft Excel worksheet, will be loaded into the appropriate database table via a custom-designed user interface Visual Basic program. Any analytical data that cannot be provided by the laboratory in electronic format will be entered manually. After entry into the database, the EDD data will be compared to the field information previously entered into the database to confirm that all requested analytical data were received.

8.6.6 Data Analysis and Reporting

The database management system will have several functions to facilitate the review and analysis of the RAL Assessment and Off-site Soils RI data. Routines have been developed to permit the user to search for analytical data from a given site for a given medium. Several output functions are also available that can be modified, as necessary, for use in the data management system.

A valuable function of the data management system will be its ability to generate tables of analytical results from the project databases. The capability of the data management system to directly produce tables reduces the redundant manual entry of analytical results during report preparation and precludes transcription errors that may otherwise occur. This data management system function creates a digital file of analytical results and qualifiers for a given medium. The file can then processed into a table of rows and columns that can be transferred to word processing software (e.g., Microsoft Word) for final formatting and addition of titles and notes. Tables of analytical data will be produced as part of data interpretation tasks and for reporting data to the IEPA.

Another function of the data management system will be to create digital files of analytical results and qualifiers suitable for transfer to mapping/presentation software. A function has been created by BBL that creates a digital file consisting of sample location number, state plane coordinates, sampling date, detected constituents, and associated concentrations and analytical qualifiers. The file can then be transferred to an AutoCAD work to plot a location's analytical data in a "box" format at the sample location (represented by the state plane coordinates).

The data management system also has the capability of producing a digital file of select parameters that exist in one or more of the databases. This type of custom function is accomplished on an interactive basis and is best used for transferring select information into several analysis tools, such as statistical or graphing programs.

8.6.7 Document Control and Inventory

BBL maintains project files at its Chicago, Illinois, and Syracuse, New York offices. Each client project is assigned a file/job number. Each file is then broken down into the following subfiles:

1. Agreements/Proposals (filed chronologically);
2. Change Orders/Purchase Orders (filed chronologically);
3. Invoices (filed chronologically);
4. Project Management (filed by topic);
5. Correspondence (filed chronologically);
6. Notes and Data (filed by topic);
7. Public Relations Information (filed by topic);
8. Regulatory Documents (filed chronologically);

9. Marketing Documents (filed chronologically);
10. Final Reports/Presentations (filed chronologically);
11. Draft Reports/Presentations (filed chronologically); and
12. Documents Prepared by Others (filed chronologically).

Hard-copy originals and electronic data deliverables, when possible, are placed in the files. These are the central files and will serve as the project-specific files for the DePue Site.